THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

OCTOBER 1927.

LVI. *On a Theory of the Magnetic Properties of Iron and other Metals* *. *By* R. H. DE WAARD, *D.Sc.* (*Utrecht, Holland*). †

A. A REMARKABLE PROPERTY OF THE MECHANISM OF MAGNETIZATION IN FERROMAGNETIC METALS.

CONSIDER a cylindrical bar of some ferromagnetic metal (=a metal showing the phenomenon of magnetic hysteresis), *e. g.* of iron, and let it be placed along the axis of a very long solenoid. When a given electric current is sent through this solenoid, the bar will find itself in a homogeneous magnetic field of known intensity H ‡ which can be changed in any way desired; the magnetization M of the bar (= the magnetic moment per c.c.) may in this way pass through a series of different values. We will suppose the bar so long that, whatever the value of M may be, the demagnetizing force (which is proportional to M) may be neglected.

Let us now start from the "normal" state, where H=M=0; we shall then be able, by suitable changes of H, to make M pass through a series of values which

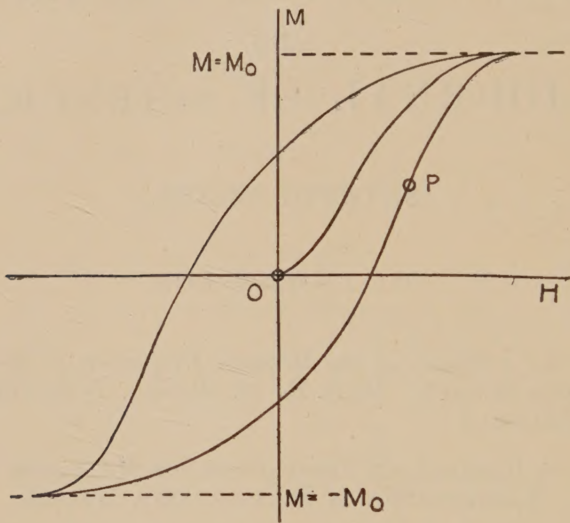
* The principles of the theory worked out in some detail in this paper have been given in the author's Dutch thesis: 'Ferromagnetisme en Kristalstruktuur.' Dissert. Utrecht, 1924. A translation in French is found in: *Archives Néerlandaises*, ser. iii. A, tome viii., 1925 ("Ferromagnétisme et structure crystalline").

† Communicated by Prof. L. S. Ornstein.

‡ All magnetic quantities will be expressed by means of the units used by Lorentz in 'The Theory of Electrons' (Leipzig and New York, 1916).

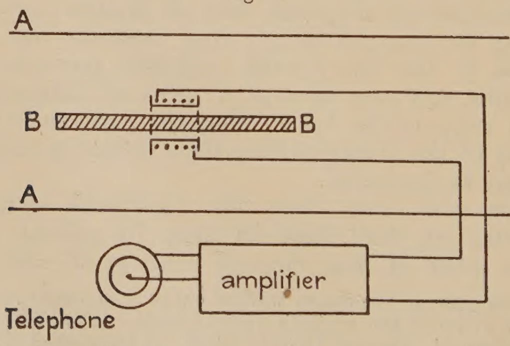
are, in their dependence on H, shown by the well-known curves of hysteresis (fig. 1).

Fig. 1.



An insight into the mechanism of such a process can be obtained from the experiments of Barkhausen*, which show that M is not only changing continuously, but also partly by small jumps. The principle of these experiments is

Fig. 2.



BB, iron bar.
AA, cross-section of the solenoid.

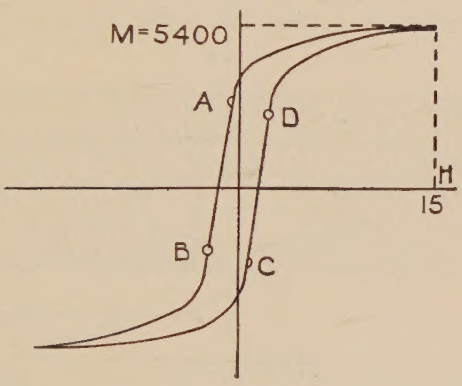
that in a small coil put round a bar like the one considered, every jump of M causes a pulse of induction which can, by means of a triode amplifier, be made detectable in a telephone (fig. 2).

* *Physik. Zs.* 1919, p. 401.

Barkhausen's experiments are repeated and extended by van der Pol *, who points out that in a certain iron bar (wire) whose curve of hysteresis is shown in fig. 3 jumps were observed in the intervals AB and CD.

These jumps must be ascribed to sudden changes of the magnetic state of certain sets of iron-crystals, and it is natural to suppose that these changes will consist of an abrupt reversal of the magnetization from positive to negative (resp. from negative to positive) values. *It is, however, easy to show that the shape of a set of crystals*

Fig. 3.—Iron.



which causes a jump of M *near* A *must be extremely prolate and that such a set must be a long row of crystals forming a sort of chain in the direction of the external field.*

For convenience we will suppose that the shape of the set is that of a rotational ellipsoid whose axis has the same direction as that of the bar. When, now, the state is realized which is indicated by A in fig. 3, and when for a moment we consider the space occupied by the ellipsoid as an empty space (without changing anything in the magnetic state of the rest of the bar), there will exist a magnetic field H_i inside of it whose intensity is easily calculated (fig. 4).

First there is the external field caused by the solenoid; its intensity

$$H = -0{\cdot}5$$

can be obtained from fig. 3. Besides that, however, the field should be considered which is caused by the parts

* Proc. Amsterdam, xxiii. p. 980 (1920).

of the bar outside the ellipsoid. The intensity of this field may be written

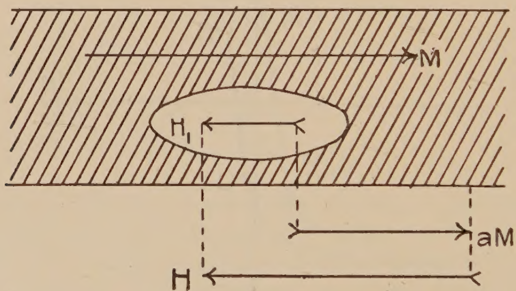
$$aM,$$

when a is the demagnetizing coefficient of the ellipsoid in the direction of the axis. The value of M, as well as that of H, can be obtained from fig. 3 (M=2500), and consequently one has

$$H_i = -0{\cdot}5 + 2500\,a.$$

Thus the set of crystals under consideration which is magnetized in the positive direction finds itself under the influence of a magnetic field of this intensity. When, however, H_i is decreased by a small quantity the magnetization assumes a negative value by a sudden jump.

Fig. 4.



It is now obvious that this would be impossible if H_i were positive, for in this case there would be no question of any tendency to such a reversal. Consequently one has

$$H_i = -0{\cdot}5 + 2500\,a < 0,$$

and one must conclude that

$$a < \frac{0{\cdot}5}{2500} \quad \text{or} \quad a < 0{\cdot}0002.$$

Now the proportion of the axes of a rotational ellipsoid for which

$$a < 0{\cdot}0002$$

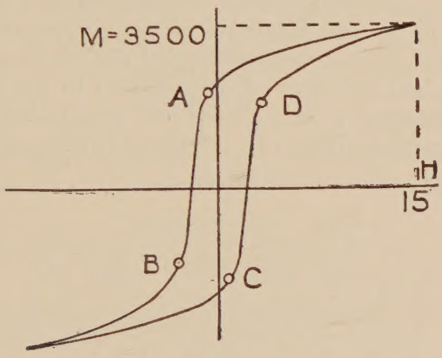
is smaller than 1 : 100. We have therefore proved that a set of iron-crystals which causes a discontinuity of M in the neighbourhood of A must be a long chain the length of which is certainly longer than 100 cross-diameters. *On first sight such a result looks very strange. It is, however, in perfect accordance with experiments.* Van der Pol also examined a bar of nickel-steel and got in that way the

M–H-curve shown in fig. 5. The same sort of argument as that used for fig. 3 in this case leads to

$$a < \frac{1}{2000} = 0{\cdot}0005,$$

which corresponds to a proportion of the axes of the ellipsoid smaller than 1 : 80. Van der Pol was then able to estimate both the length and the cross-section of a set of iron-crystals which gave rise to certain discontinuities of M. In order to find the length of a set he registered,

Fig. 5.—Nickel-steel.



with the help of two galvanometers, the pulses of inductions caused by these discontinuities in two different coils (like the one of fig. 2) which he placed round the bar at some distance one from the other ; it appeared that certain discontinuities were still synchronously registered when this distance was as great as 7 cm. Hence the sets of crystals causing these discontinuities must have had a length of at least 7 cm. From the magnitude of the discontinuities it was possible to deduce that the cross-diameter was of the order of 0·05 mm., and these two numbers give rise to a proportion of axes of

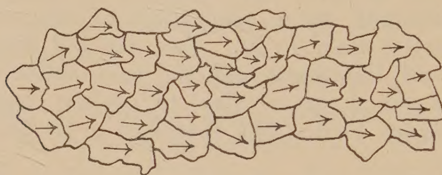
$$0{\cdot}005 : 7 = 1 : 1400,$$

much smaller still than the proportion 1 : 80 which was *a priori* considered to be improbably small.

In order to make the obtained result more acceptable, we shall proceed to a more detailed consideration of the mechanism of the process of magnetization. We know that an iron bar must be considered as an aggregate of iron-crystals. When such an aggregate is under the

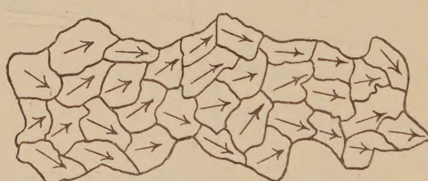
influence of a strong magnetic field H, every crystal will possess a nearly saturated magnetization in the direction of the field (fig. 6 *a*). When now this field is decreased until

Fig. 6 *a*.



$H=0$ the magnetic state of the crystals will to a great extent be determined by the structure of the aggregate, with this condition, that the magnetization will still show a preference for the original direction of H and that in no crystal shall there be already a component of magnetization in the opposite direction (fig. 6 *b*). During further decrement of

Fig. 6*b*.



H components of magnetization in the negative direction will gradually appear, and this does not only occur continuously, but also, as we have seen, by jumps.

Let us now consider a certain crystal K. This crystal is under the influence of the external field and under that of the surrounding parts of the aggregate. When K is of the same order of magnitude in all directions these surrounding parts will cause inside the space of K a magnetic field of the order of 1/3 M (fig. 7 *a*). Together with the external field this gives rise to a field

$$H_i = 1/3\,M + H$$

acting on K. When now we keep in mind that a changing of the magnetization of K to a negative value without appreciable changes in the neighbourhood will only be possible when

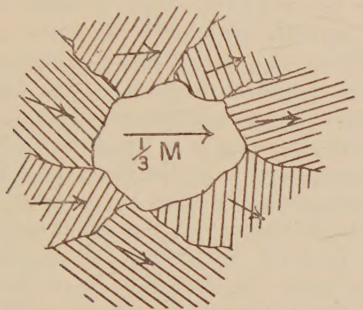
$$H_i < 0,$$

we see that such a change only comes into question when

$$H < -1/3\,M.$$

For a simultaneous reversal of the magnetization in a long row R of crystals like K the conditions are much sooner favourable. When, for instance, such a row consists of 50 crystals and when consequently its length is about

Fig. 7 *a*.



50 times the mean cross-diameter, the surrounding aggregate causes inside R a magnetic field of the order of

$$0{\cdot}0015\,\mathrm{M} \quad (\text{fig. } 7\,b),$$

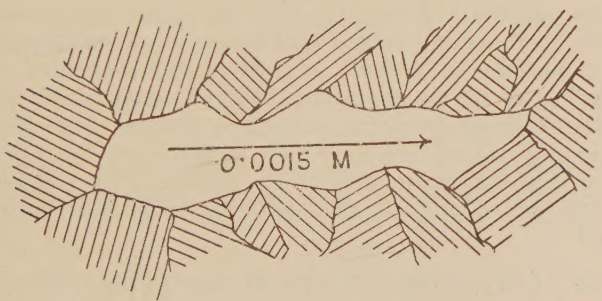
and one has

$$\mathrm{H}_i = 0{\cdot}0015\,\mathrm{M} + \mathrm{H}\,;$$

therefore a reversal of the magnetization of R may be possible as soon as

$$\mathrm{H} < -0{\cdot}0015\,\mathrm{M}.$$

Fig. 7 *b*.



In general we may say that the more prolate the shape of a complex of crystals is, the sooner the complex will show a tendency to a simultaneous and concurrent jump of the magnetizations in the different parts. It is however clear, that the constitution of the different chains with magnetic coherence largely depends on the structure of the aggregate.

The mechanism of the process of magnetization in the interval AB may now be imagined to be that abrupt changes of the magnetization into negative values will in the beginning only occur in extremely prolate sets of crystals, but after a time also in chains of smaller length. There is, however, some reason to suppose that there are also crystals which do not show such a sudden change and whose magnetizations continuously decrease from positive to negative values (apart from small discontinuities caused by real jumps of crystals in the neighbourhood); these changes will as well as the real jumps occur for the greater part in the interval AB. When B is reached it seems probable that no crystal is left with a component of magnetization in the positive direction of H; and when, by further decrement of H, M is still more decreased, this must be ascribed to a forcing of magnetizations in the negative direction of H. The picture of the mechanism of the process of magnetization given in this section, which is evidently also applicable to the other branch of the curve of hysteresis, will be further illustrated and specified in the following sections.

B. A General Theory of Ferromagnetism with simple applications.

§ 1. *Definitions and Fundamental Formulæ.*

The magnetic force H in any point of space is the resultant of two magnetic forces H_e and H_m which are caused by electric currents and magnetized bodies respectively.

We consider a system of ferromagnetic bodies under the influence of the magnetic field of constant or slowly varying electric currents. Such a system represents a certain amount of energy which depends on the currents and on the magnetic state of the bodies. We will assume that the part of this energy depending on M is given by the formula

$$E = -\int (H_e \, . \, M) \, d\tau - \tfrac{1}{2}\int (H_m \, . \, M) \, d\tau + \tfrac{1}{2}\int \theta M^2 \, . \, d\tau, \quad . \quad (1)$$

in which the integrals must be taken over the space occupied by the magnetized bodies. The first term of this equation does not require much explanation: the magnetic moment of an element of volume $d\tau$ with a magnetization M is $M \, . \, d\tau$, and the energy of such a magnetic moment with respect to the electric currents (which cause the field H_e) is

$$-(H_e \, . \, M) \, d\tau,$$

when $(H_e . M)$ denotes the scalar product of the vectors H_e and M.

The second and third terms must be considered in mutual connexion. At first sight it might seem that the energy of an element $d\tau$ with respect to the rest of the magnetic bodies is equal to

$$-(H_m . M)\, d\tau ;$$

in reality, however, it differs from that quantity because H_m is not the magnetic force caused inside $d\tau$ by the surrounding substance only but contains also the magnetic field caused by $d\tau$ itself. When nevertheless we make use of this expression and when we ascribe half of it to the element $d\tau$ and the other half to the rest of the magnetic bodies, we must keep in mind that the third term must account for some compensation. In a given element $d\tau$ this compensation can evidently only depend on M.

Except for this compensation the third term will account for the supposition that (even apart from the energy with respect to its own field) an element $d\tau$ of a magnetic body contains a certain amount of energy in virtue of the fact of its magnetization. The simplest assumption which in this respect can be made is this, that the integrand of the third term

$$\tfrac{1}{2}\int \theta M^2 . \, d\tau$$

is proportional to the square of the local magnetization: θ is a constant which must be expected to have different values in different ferromagnetic substances.

By these remarks the fundamental formula (1) seems to be sufficiently explained.

§ 2. *Application of the Theory to Homogeneous Ellipsoids in Homogeneous Magnetic Fields.*

Consider an ellipsoid consisting of a homogeneous ferromagnetic substance and let it be placed in a homogeneous magnetic field H_e (caused by given electric currents) with one of the axes (Ox) in the direction of this field. When we denote the demagnetizing coefficients in the directions Ox Oy Oz of the axes of the ellipsoid by a, b, and c $(a+b+c=1)$ and when we suppose a homogeneous magnetization M throughout the ellipsoid, the components of H_m along the axes are

$$-aM_x, \quad -bM_y, \quad -cM_z,$$

and the energy per cm.³ of the ellipsoid may be written:

$$E = -H_e M_x + \tfrac{1}{2}(aM_x^2 + bM_y^2 + cM_z^2) + \tfrac{1}{2}\theta(M_x^2 + M_y^2 + M_z^2).$$

Putting
$$a+\theta = A, \quad b+\theta = B, \quad c+\theta = C, \quad . \quad . \quad . \quad (2)$$
we get
$$E = -H_e M_x + \tfrac{1}{2}(AM_x^2 + BM_y^2 + CM_z^2). \quad . \quad . \quad (3)$$

With the help of this formula we will now examine how, in different cases, M behaves when H_e is varied. In accordance with a well-known experimental fact in ferromagnetism we will, however, suppose that the absolute value of M is limited and can never exceed a certain magnetization of saturation M_0. Thus we have the condition:
$$M_x^2 + M_y^2 + M_z^2 \leqq M_0^2 \text{*}. \quad . \quad . \quad . \quad . \quad (4)$$

Our task is now to find the sets of values of M_x M_y M_z which satisfy the condition (4) and for which the energy E has minimum values. This problem is very much simplified when we suppose that the axis Oz of the ellipsoid is shorter than Oy, which is evidently possible without any loss of generality. We then have

$$b \leqq c, \text{ and consequently } B \leqq C,$$

and it is easily seen that under these circumstances we may put
$$M_z = 0.$$

When, indeed, M has a component perpendicular to Ox the expression
$$\tfrac{1}{2}(BM_y^2 + CM_z^2)$$
and consequently the energy E can only have minimum values when this component has the direction of the axis Oy. Instead of (3) we thus get the formula

$$E = -M_x H_e + \tfrac{1}{2}(AM_x^2 + BM_y^2), \quad . \quad . \quad . \quad (3\,a)$$

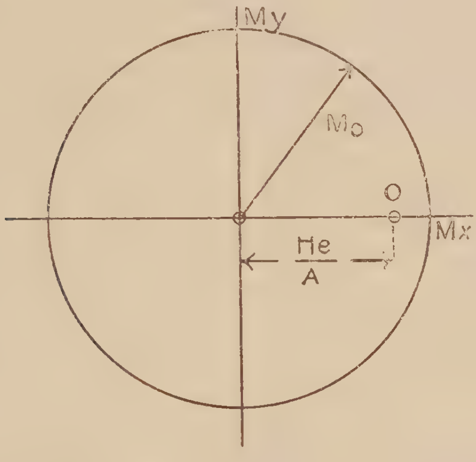
which may be written
$$E = \tfrac{1}{2}A\left(M_x - \frac{H_e}{A}\right)^2 + \tfrac{1}{2}BM_y^2 - \frac{H_e^2}{2A}.$$

When H_e and E are given, this equation expresses a relation between M_x and M_y which, in a M_x–M_y-diagram,

* A condition of this kind is lacking in the general theory of magnetism given by Helmholtz, 'Vorlesungen über theoretische Physik,' iv. § 52, which is based on much the same principles as the one explained in this paper. This theory is for this reason unable to account for the phenomena of ferromagnetism. It cannot explain diamagnetic phenomena either (as is wrongly supposed), since it shows itself in contradiction to these phenomena as soon as stability is considered.

is represented by a conic whose centre is the point $O\left(\frac{H_e}{A}, 0\right)$ (fig. 8). Different values of E correspond (as long as H_e is kept constant) to different individuals of a set of concentric conics.

Fig. 8.



The condition (4) may be replaced by

$$M_x^2 + M_y^2 \leqq M_0^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4\,a)$$

and the pairs of values of M_x and M_y satisfying it are in the M_x-M_y-diagram represented by the points inside and on the circle C whose radius is M_0 and whose centre is the origin.

Let the value of H_e be given. In order to get the values of M_x and M_y which satisfy the condition (4 *a*) and for which E is smaller than for slightly different values satisfying the same condition, we must try to find, in the M_x-M_y-diagram, the points P which are situated

(*a*) inside or on C, and

(*b*) on an E-conic for which E is smaller than for the E-conics which pass through the space inside C in the neighbourhood of P.

When doing this we are led to the consideration of four different cases:

I. $B > 0$, $A < 0$;
II. ,, $A > 0$;
III. $B < 0$, $A < B$;
IV. ,, $A > B$.

The first of these cases will be treated in some detail. Of the treatment of the other cases, which is very much the same, only the results will be mentioned.

Treatment of Case I. $(B>0, A<0)$.

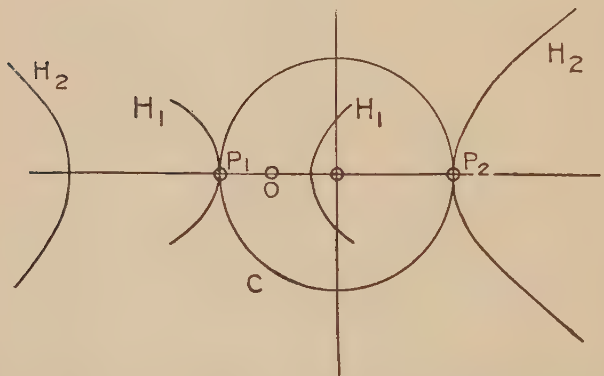
Let H_e have a given positive value: the point $O\left(\frac{H_e}{A}, 0\right)$ of fig. 8 is then situated on the left side of the origin. The E-conics determined by the equation (3 *a*) are hyperbolæ of which the axis of M_x is the real axis. The smaller values of E correspond to the more excentric hyperbolæ.

When

$$H_e < -AM_0$$

it is clear that there are two points P_1 and P_2 (fig. 9)

Fig. 9.



satisfying the conditions (*a*) and (*b*) mentioned above. These points correspond to the states

$$P_1: \quad M_x = -M_0, \quad M_y = 0,$$
$$P_2: \quad M_x = M_0, \quad M_y = 0.$$

When

$$H_e > -AM_0$$

the point P_1 falls out of consideration and the one point P which is left corresponds to the state

$$M_x = M_0, \quad M_y = 0.$$

As analogous results are obtained when H_e is negative, we are led to the following conclusions:—

"When $H_e > -AM_0$ we must have $M_x = M_0$; the magnetization is then saturated in the positive direction of Ox.

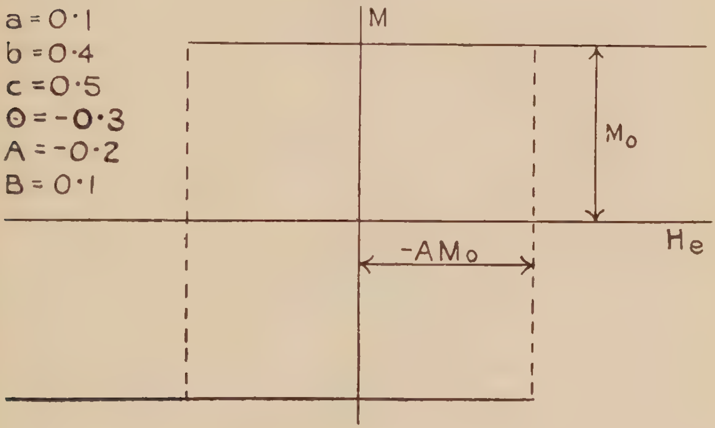
As H decreases this magnetization will persist as long as

$H_e > AM_0$, but as soon as $H_e = AM_0$ it will suddenly change into saturation in the negative direction ($M_x = -M_0$) and then persist as H_e decreases further.

When, on the contrary, H_e is increasing from a value $< AM_0$, the magnetization will again change into positive saturation at the moment that $H_e = -AM_0$."

The behaviour of M_x expressed in these sentences is graphically shown in the M_x–H_e'-diagram of fig. 10 *a*. We

Fig. 10 *a*.



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 5.$$

have evidently to do with a case in which the phenomenon of magnetic hysteresis is present in its simplest form. The coercive force is

$$H_c = -AM_0.$$

Cases II. ($B > 0$, $A > 0$) *and III.* ($B < 0$, $A < B$).

The results of the treatment of these cases are respectively shown in the M_x–H_e-diagram of figs. 11 *a* and 12 *a*.

Case IV. ($B < 0$, $A > B$).

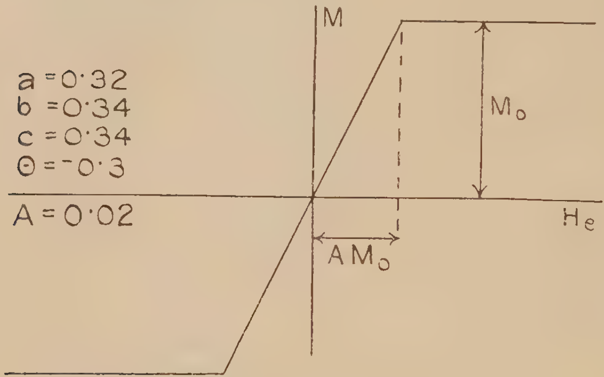
This case is rather uninteresting. When $H_e = 0$, one has

$$M_x = 0, \quad M_y = \pm M_0.$$

When now H_e increases the magnetization keeps its saturation value M_0, but its direction changes in such a way

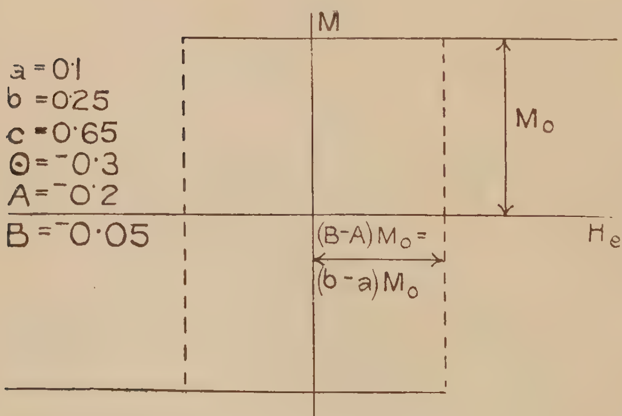
that the angle it includes with the axis Ox continually decreases and becomes zero on the moment that H_e surpasses a certain value. When, after this, H_e decreases, essentially the same states are realized in reversed succession.

Fig. 11 *a.*



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 25.$$

Fig. 12 *a.*



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 5.$$

Negative values of H_e evidently lead to analogous results. In order to make these results comprehensible we will add a few remarks. As $A > B$ we have $a > b$, which implies

that the axis Ox of the ellipsoid considered is, just as the axis Oz (see p. 650), shorter than the axis Oy. Thus the axis Oy is the longest of the three, and in the state without an external field ($H_e=0$) the magnetization is saturated in the positive or in the negative direction of this longest axis. By applying an external field along the axis Ox one can make this magnetization deflect to the x-direction.

As in practice of ferromagnetic measurements, however, use is generally made of long wires or bars to which external fields are applied in the direction of greatest length, a thorough discussion of the case under consideration is of no importance.

Comparative Discussion of the Cases I., II., and III.

A consideration of the cases I., II., and III. immediately shows that the presence or absence of hysteresis only depends on the value of A; when A is negative there will be hysteresis, and when it is positive there will be none.

Now we know that in virtue of the formula

$$A = a+\theta$$

A depends both on the shape of the ellipsoid considered and on the material of which it is composed; thus the question whether a given ferromagnetic body will show the phenomenon of hysteresis can only be answered when not only the material but also the shape of the body is taken into account.

In practice, however, this is probably never done: it is generally admitted that there exist substances which show magnetic hysteresis and other substances which do not, and that the shape is, in this respect, of no essential importance. Or, in more definite terms: it is generally supposed that in a given substance the behaviour of the magnetization M in any point only depends on that of the local magnetic field,

$$H = H_e+M_m,$$

and that in the relation between M and H the shape of the magnetic body considered does not appear *.

The reason of this generally accepted wrong supposition

* The relation between M and H_e, however, is always supposed to depend and in fact does depend on the shape of the body. Thus in an oblate rotational ellipsoid of iron, magnetized along the axis, the demagnetizing force H_m is so large that an external field H_e of extreme intensity is necessary to bring about a total field H inside the ellipsoid which is large enough to give rise to a reasonable magnetization and a perceptible hysteresis. For this reason measurements of hysteresis are always carried out on long wires or bars.

will be explained in connexion with the formula (4 a):

$$E = -M_x H_e + \tfrac{1}{2}(AM_x^2 + BM_y^2).$$

The ordinary conditions of equilibrium are:

$$\frac{\partial E}{\partial M_x} = -H_e + AM_x = 0 \quad \text{or} \quad AM_x = H_e,$$

$$\frac{\partial E}{\partial M_y} = BM_y = 0 \quad \text{or} \quad M_y = 0.$$

When we now neglect the conditions of stability we find

$$H_m = -aM_x,$$

and consequently

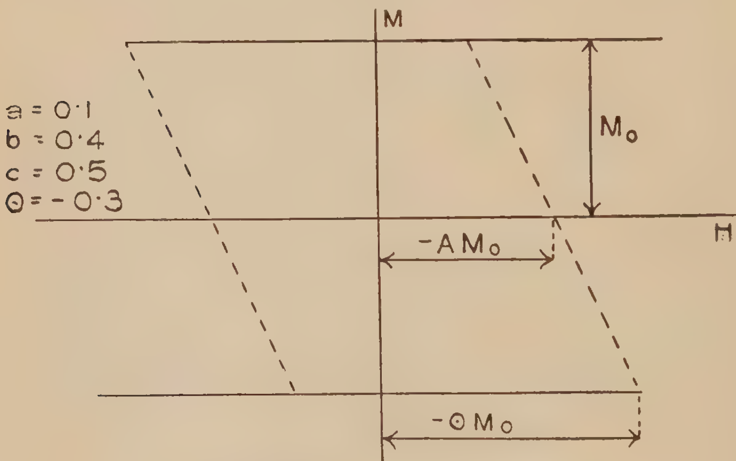
$$H = H_e + H_m = AM_x - aM_x = \theta M_x.$$

Now, in the formula

$$H = \theta M_x$$

there is no quantity which has to do with the shape of the

Fig. 10 b.



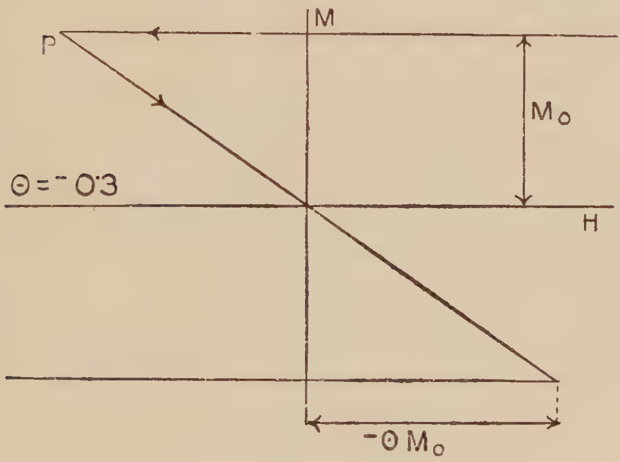
$$\frac{\text{unit of length ou axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 5.$$

ellipsoid considered; thus, when stability is neglected one gets the impression that in a given ferromagnetic substance (that is to say, when θ is given) the magnetization only depends on the total magnetic field H.

That in reality this is not the case is clearly seen when the M_x–H_e-diagrams of figs. 10 a, 11 a, and 12 a are transformed into M_x–H-diagrams; these M_x–H-diagrams are

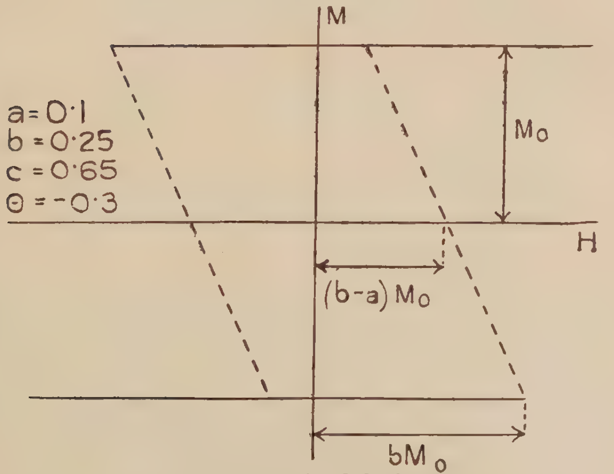
shown in figs. 10 *b*, 11 *b*, and 12 *b*, and are by no means identical. In order to make them as illustrative as possible

Fig. 11 *b*.



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 5.$$

Fig. 12 *b*.



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 5.$$

of the influence of the shape of a body on its magnetic properties, they have been drawn in such a way that the

value of θ (or the nature of the substance in question) is the same in the three cases ($\theta = -0{\cdot}3$). Evidently the occurrence of hysteresis is more probable the more prolate the ellipsoid is.

We thus have been led to the conclusion that certain values of θ may give rise to three different kinds of M_x–H_e-diagrams. This is, however, not the case for every value of θ. When, for instance, θ is positive, A, B, and C are positive as well and we have always to do with a M_x–H-diagram like that of fig. 11 *b*; hysteresis is impossible. When on the contrary $\theta < -1/3$, there is at least one of the coefficients A, B, and C which is <0 (because at least one of the coefficients a, b, and c is $\leq 1/3$), and there is hysteresis in every case (except in that of a sphere), both of the diagrams 10 *a* and 12 *a* being possible*. When $-1/3 < \theta < 0$, every one of the three cases of figs. 10 *a*, 11 *a*, and 12 *a* is possible; presence or absence of hysteresis depend on the shape of the ellipsoid considered.

It will be clear that we have treated in this paragraph the simplest cases † of the simplest theory of ferromagnetism one can think of. Nevertheless these simple cases were in some respects more complicated than is ever admitted in any case occurring in practice. We may therefore conclude that it is absolutely necessary that in the interpretation of experiments on ferromagnetism the following facts are taken into account:—

1. That it is probable that the magnetic properties of bodies (for instance, presence or absence of magnetic hysteresis) will essentially depend on the shape of these bodies; and
2. That there is no reason to believe that the behaviour of the magnetization will merely depend on that of the internal field H.

* See footnote on p. 650. When one would try to describe the phenomena of diamagnetism with the help of the formula $H = \theta M_x$, it would be necessary to introduce strongly negative values of θ; even for bismuth, the substance with the strongest diamagnetism, one would find $\theta = -560{,}000$. In the present theory such a value of θ would, however, necessarily lead to the presence of magnetic hysteresis, and the only stable states would be those with saturated magnetization. The theory is therefore unable to explain the phenomena of diamagnetism.

† The conditions of these simple cases have been recently realized in experiments by W. Gerlach (*Zs. f. Physik*, xxxviii. p. 828, 1926) and by K. Honda and S. Kaya (Sc. Rep. of the Tohoku Imp. Univ. xv. 6, p. 721, 1926) on the magnetic properties of specimens of iron consisting of single crystals. In a following paper I hope to discuss the results of these experiments in connexion with the present theory.

§ 3. *Two Ellipsoids.*

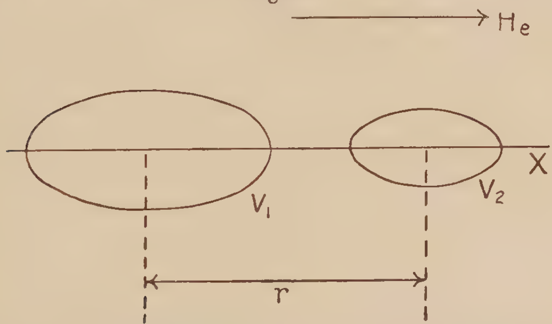
Among the many different views concerning the mechanism of the process of magnetization in ferromagnetic substances there is a very plausible one which we will first briefly explain. It will then be easy to show that in reality it is certainly wrong.

The sort of argument in question is the following :

" An iron bar is an aggregate of a great number of iron crystals. The magnetic state of this bar must consequently be considered as the sum of the magnetic states of these crystals. If the bar shows the phenomenon of magnetic hysteresis the crystals or at least a number of them must do the same, and when the magnetization of such a crystal is plotted against the external field H_e or against the total field H (in a very long bar these fields hardly differ) one has to expect a loop of hysteresis."

Thus far the argument is correct. It is, however, pursued in such a way that it is believed to be obvious that the

Fig. 13.



crystal will show the same loop when it is loosened from the surrounding substance and independently examined in a magnetic field.

We will show that this supposition is by no means probable. For this purpose we will apply our theory to a system of two uniform ellipsoids, whose longest axes are in the same straight line. We suppose that each of these ellipsoids, when considered on its own, does not show any hysteresis : this will be the case if $0<A<B<C$. The volumes of the ellipsoids will be denoted by v_1 and v_2 $(v_1>v_2)$. When now the distance r of their centres is so large that the field of the first ellipsoid inside the second one may be considered to be homogeneous, and inversely, and when an external field H_e is applied in the (x-)direction

of the line joining the centres, the total energy may be written :

$$\begin{aligned} E = {} & \frac{v_1}{2}(AM_{1x}^2 + BM_{1y}^2 + CM_{1z}^2) \\ & + \frac{v_2}{2}(AM_{2x}^2 + BM_{2y}^2 + CM_{2z}^2) \\ & - \frac{v_1 v_2}{4\pi r^3}(2M_{1x}M_{2x} - M_{1y}M_{2y} - M_{1z}M_{2z}) \\ & - H_e(v_1 M_{1x} + v_2 M_{2x}). \end{aligned}$$

As there are two accessory conditions to be considered,

$$M_{1x}^2 + M_{1y}^2 + M_{1z}^2 \leqq M_0^2 \quad \text{and} \quad M_{2x}^2 + M_{2y}^2 + M_{2z}^2 \leqq M_0^2,$$

it is a rather complicated matter to find the sets of values of

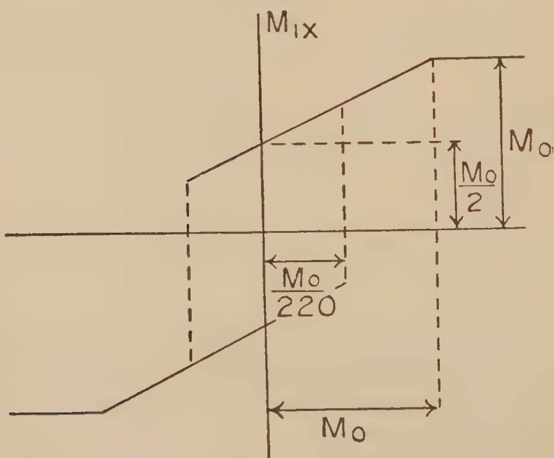
$$M_{1x} \; M_{1y} \; M_{1z} \; M_{2x} \; M_{2y} \; M_{2z}$$

for which E has a minimum value ; we will therefore only give the main results of the analysis :—

" Magnetic hysteresis will be present if

$$A < \frac{\sqrt{v_1 v_2}}{2\pi r^3};$$

Fig. 13 *a*.



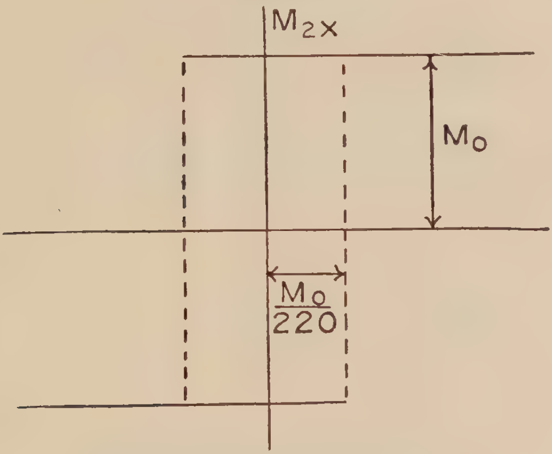
$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}} = 100.$$

this is, for instance, the case when

$$\frac{v_1}{2\pi r^3} = 0{\cdot}09, \quad \frac{v_2}{2\pi r^3} = 0{\cdot}01, \quad A = 0{\cdot}02.$$

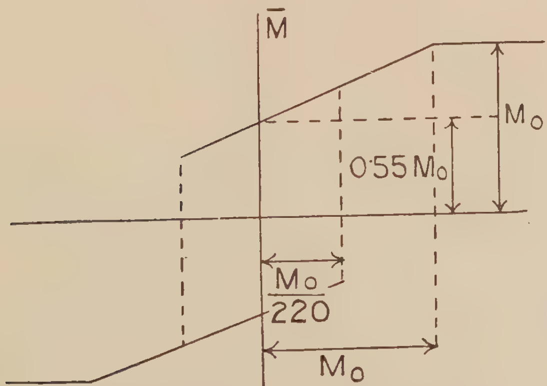
When this case is more closely considered it appears that M_{1x} and M_{2x} depend on H_e in the ways shown in figs. 13 *a*

Fig. 13 *b*.



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}}=100.$$

Fig. 13 *c*.



$$\frac{\text{unit of length on axis of abscissæ}}{\text{unit of length on axis of ordinates}}=100.$$

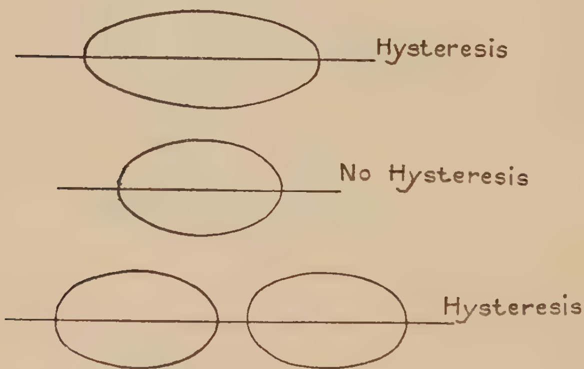
and 13 *b*; the other components of M_1 and M_2 are always $=0$. In fig. 13 *c* the mean magnetization

$$\overline{M}=0{\cdot}9M_{1x}+0{\cdot}1M_{2x}$$

is shown in its functional dependence on H_e."

We thus see that it is possible that magnetic hysteresis is found in a system of two ellipsoids which do not show any phenomenon of this kind when they are considered separately. After what has been said in § 2, however, this is by no means surprising. In this paragraph we have found that a prolate ellipsoid e_1 of a certain substance may show magnetic hysteresis, while a less prolate ellipsoid e_2 of the same material is free from this property. It can therefore hardly be considered as striking that a system of two ellipsoids e_2 placed one behind the other has a property in common with e_1 which is absent in e_2 (fig. 14).

Fig. 14.



This result is of great importance for our further consideration. It shows that an iron bar may possess the property of magnetic hysteresis even when this phenomenon does not occur in any of the composing crystals. Now, in the following section we shall be obliged to ascribe to a metal like iron a value of θ of such a kind that in a single rotational ellipsoid of this substance a proportion of axes of about 1 : 100 would be necessary to give rise to any hysteresis; thus it is of interest to know that there is no reason to abandon the theory because needle-shaped crystals of this kind will hardly be present in ordinary iron. The magnetic hysteresis of iron may be just as well caused by the reversal of the magnetization in the long chains of crystals considered in the first section; in their magnetic properties these chains will certainly show some analogy with extremely prolate homogeneous ellipsoids.

C. Estimation of the Values of θ for Iron, Nickel, Cobalt, and some species of Steel.

Our aim is to find the values which must be ascribed to the quantity θ in metals like iron, nickel, etc.

In the first place these values must be negative, for in section B we have found that otherwise hysteresis is impossible.

In order to obtain numerical approximations of θ it is necessary to consider more closely the properties of the chains of crystals which have been so frequently mentioned. As to the length of these chains in some iron or nickel wire we must suppose that they will be as long as is consistent with the structure of the wire; or in more definite terms: when there exists, in the wire, a row of crystals which passes through it over a long distance without showing marked discontinuities, it is probable that, in the processes of magnetization and demagnetization along the axis of the wire, this row must be considered as a magnetic unit. The fact that in nickel-steel chains of about 7 cm. of length have been found experimentally is certainly in favour of this view, which has appeared to be probable for theoretical reasons.

At the end of the second section we have pointed out that the magnetic properties of these chains are, to a certain extent, comparable to those of prolate homogeneous ellipsoids. It is, however, clear that when in a chain of crystals and in a homogeneous ellipsoid of about the same shape θ has the same negative value, and when both show the phenomenon of hysteresis, the stronger hysteresis will be found in the ellipsoid. This is easily seen when we keep in mind that during the performance of a loop of hysteresis a series of states are realized which possess only a conditional stability; when in these states perturbations of sufficient amount are applied other states will arise in which the energy has smaller values. It is then at once evident that in a chain of crystals with its inevitable discontinuities a way to the lower stages of energy is more easily found than in a homogeneous ellipsoid of about the same shape, and that in such a chain the magnetization will be more inclined to conform to the external field. When, nevertheless, in the following discussion we shall treat a chain as a homogeneous ellipsoid and when, in that supposition, we shall find an estimation of the value of θ, we must keep in mind that this estimation will be certainly too large and that the real value of θ will be more strongly and perhaps much more strongly negative.

We first consider the jump of M which occurs in the state indicated by the point A in fig. 3. In the first section we have found that this jump must be ascribed to the reversal of the magnetization in a very long chain of crystals. We will suppose that this chain is just as long as the iron wire itself; it is then unnecessary to consider the magnetic state of the surrounding material and we have only to do with the external field, which has, in the moment of the jump, an intensity of $-0·6$ units *. The magnetization of saturation M_0 being about 5400 units *, this leads, by an application of the case of fig. 10 a, to a value of A of

$$A = a + \theta = \frac{-0·6}{5400} = -0·0001;$$

an application of the case of fig. 12 a would be impossible, because $b-a$ is, in virtue of the prolateness of the chain, of the order of $-0·5$ instead of $-0·0001$.

When we now take into account the fact that a is of the order of 0·0002 (see p. 644) we find

$$\theta \text{ of the order of } -0·0003;$$

it has already been stated, however, that this estimation is certainly too high, and that the real value of θ will be more strongly negative.

We now consider the jump occurring in the state indicated by B, and we suppose that this jump is caused by the reversal of the magnetization in a rotational ellipsoid whose coefficient of demagnetization in the direction of the axis is a; this direction will be the same as that of the axis of the wire and that of the external field. The surrounding substance will then, in the space occupied by the ellipsoid (see fig. 4) cause a field

$$a M = -2000\,a\,*,$$

which, in addition to the external field of -2 units *, leads to a total field of

$$-2000\,a - 2 \text{ units},$$

and consequently, by application of the case of fig. 10 a, to the result

$$A = a + \theta = -\frac{-2000\,a - 2}{5400}$$

or $$1·4\,a + \theta = -0·0004.$$

* This value is obtained from fig. 3.

In the first place, this result shows that

$$\theta < -0{\cdot}0004,$$

which is quite consistent with the former estimation ; in this case, however, it is necessary to suppose that the chain causing the jump in B has a small a and consequently a considerable prolateness. The absolute necessity of the formation of these long chains was, besides this, included in the small absolute value of θ provided by the first estimation : even if this value were 100 times too small and if in reality θ were $-0{\cdot}03$, even then a homogeneous rotational ellipsoid would only show hysteresis when the proportion of axes were smaller than 1 : 9.

As to the order of magnitude of the real value of θ, we notice that in connexion with the formula

$$\theta < -0{\cdot}0004,$$

we might suppose that θ is of the order of $-0{\cdot}001$. In this way, however, the lack of homogeneity of the chain considered would not have been taken into account, and consequently it is advisable to suppose that in reality θ is of the order of about $-0{\cdot}001$ or $-0{\cdot}01$.

It will be clear that a small absolute value of θ of this kind will correspond to but a very moderate disposition on the part of the crystals to form coherent chains, for these chains must be very long and besides that radical discontinuities must be absent. Thus a considerable number of crystals will not co-operate in any chain and will have their magnetic states changed in a continuous way (apart from small discontinuities induced by primary jumps of the magnetization in chains in the neighbourhood). It is certain that an important part of the changes of the magnetization of the total wire, both inside and outside the intervals AB and CD, must be ascribed just to these crystals.

By application of the same sort of argument as that used in the discussion of the iron wire, estimations of the value of θ have been effectuated for a specimen of nickel-steel examined by van der Pol (see fig. 5), for a piece of very hard steel examined by Ewing *, and for nickel † and cobalt ‡. In the last three cases the estimations are based upon curves of hysteresis of which the intervals AB and CD are unknown and had to be determined by comparison with the known intervals in figs. 3 and 5. In all the cases

* 'Magnetic Induction in Iron and other Metals' (New York, 1894), p. 84. † *Ibid.* p. 87. ‡ *Ibid.* p. 89.

mentioned one finds that θ must be of the order of about $-0{\cdot}1$ or $-0{\cdot}01$.

These numbers will be considered in connexion with the two other quantities concerning ferromagnetic phenomena given in the following table :—

Metal.	Order of magnitude of θ.	Initial susceptibility.	H_c/M_0.
Iron	$-0{\cdot}001$ to $-0{\cdot}01$	185	0·000,25
Nickel-steel	$-0{\cdot}01$ to $-0{\cdot}1$	—	0·000,57
Hardened steel ...		50	0·003,6
Nickel...............		40	0·001,6
Cobalt...............		75	0·001,3

1. *The initial susceptibility.*

In the fundamental formula (1) the specific properties of the material considered only enter in the term

$$\tfrac{1}{2}\int \theta M^2 d\tau.$$

It is clear that the smaller the absolute value of θ is, the smaller the influence of this term will be. Thus it is evident that a small absolute value of θ will correspond to a great tendency of the magnetization to conform to the external field, that is to say, to a large initial susceptibility.

As the table shows, this conclusion is in good accordance with experimental data.

2. *The coercive force expressed in terms of the magnetization of saturation* (=the quantity H_c/M_0).

The table shows that the larger absolute values of this quantity correspond to the stronger negative values of θ. This is just what we should expect from theoretical considerations. For we know that in a chain of crystals of given length these stronger negative values of θ give rise to the larger values of the quantity $\frac{H_c}{M_0}$ for the chain (see fig. 10 a):

$$\frac{H_c}{M_0} = -A = -a - \theta.$$

Finally an important point in the process of magnetization needs discussion. It has been said that in the cases of figs. 3 and 5, jumps of the magnetization have been observed

by van der Pol in the intervals AB and CD. If our theory is correct it is, however, necessary that greater or smaller jumps also occur beyond these intervals: otherwise AB and CD would be the only parts of the two branches of the curve of hysteresis which do not coincide. Meanwhile it should be observed that not every jump is necessarily connected with a complete reversal of the magnetization in some chain of crystals; it could as well be caused by changes of the direction of the magnetization in some crystals over angles smaller than 90°.

In the cases of figs. 3 and 5, processes of this kind must be expected to occur in the descending branch in the interval on the left of B and in the ascending branch in the interval on the right of D.

LVII. *The Effect of the Acidity of the Support on the Structure of Monomolecular Films.* By Hans Egnér *and* Gunnar Hägg *.

FROM the investigations of Langmuir and Adam it is well known that the properties of a monomolecular film spread on water show a sudden change at a certain acidity of the supporting water. Adam † found, for instance, that a film of palmitic acid under low lateral pressure occupied a larger area per molecule when the pH of the water was less than 5·5, than when it was above that point. This critical acidity proved to be almost the same for all films of fatty acids. (On an average corresponding to a hydrogen ion concentration of 10^{-5} N.)

Adam explains this change in area by assuming two different structures of the film. In the case of fatty acids the attraction between the carboxyl groups and the support is supposed to increase as the hydrogen ion concentration in the latter decreases. When this concentration is above 10^{-5} N, the molecules arrange themselves in two levels, one deeper and one higher, the head groups of the higher molecules fitting into the recesses between head and chain of the deeper ones. The results of Adam indicate that in this case the packing is so close that the carbon chains are in contact with one another.

So far as the authors know no attempt has been made to explain just *why* such a sudden change in attraction takes

* Communicated by Prof. F. G. Donnan, F.R.S.

† Proc. Roy. Soc. A, xcix. p. 336 (1921).

place at a certain acidity, *why* this acidity for films of fatty acids corresponds to a pH of about 5, and *why* this critical acidity seems to be practically the same for all fatty acids, although the absolute attraction between these acids and water must vary considerably even for the higher ones. It appeared to us, however, that the questions just asked might be answered, easily and in a quite natural way, if the dissociation equilibria of the film-forming substances are taken into consideration. This will be done in the following brief discussion of the system fatty acid-water, which is the only one for which data are available. As will be pointed out below, there is reason to believe, however, that the same phenomena take place in other systems of the same character.

According to the law of mass action, the relation between pH and the degree of dissociation (α) of an acid is governed by the well-known equation

$$\frac{\alpha}{1-\alpha}=10^{p\mathrm{H}-p\mathrm{K}a},$$

where $p\mathrm{K}a$ is the negative logarithm of its dissociation constant. If we proceed along the pH axis, the transformation from the undissociated to the dissociated form is most rapid when $p\mathrm{H}=p\mathrm{K}a$, where the curve shows an inflexion point, and the relative proportion of these two forms is changed from 10 to 1/10, when pH varies from $p\mathrm{K}a-1$ to $p\mathrm{K}a+1$. This rapid change is familiar to most chemists from work with monobasic indicators; their usefulness is limited to a pH-region of about 2 units.

Is the same equation valid for molecules in a monomolecular layer? It is difficult to see why it should not be so. If we look at a single molecule in the layer, its neighbours may exert some influence on its tendency to send out or take in hydrogen ions, but the influence cannot be very strong. In any case, it cannot be nearly so strong as the influence of a polar group inside the same molecule, and in this case we know that the effect of a second carboxyl group is not very great even in a small molecule, it may be dissociated or not. Succinic acid, for example, has a $p\mathrm{K}a_1$ of 4·2 and a $p\mathrm{K}a_2$ of 5·6, whereas propionic and butyric acids both have a $p\mathrm{K}a$ of about 4·9.

The dissociation constants of fatty acids with a higher molecular weight than that of Nonylic (Pelargic) acid have not been determined, owing to their very small solubility in water (which for nonylic acid corresponds to a mol fraction of $1{\cdot}4\times10^{-5}$, and for myristic acid with 14 carbon atoms

to a mol fraction of ca. 10^{-8}). The following table shows $p\mathrm{K}a$ for the lower acids at 25° C.

TABLE I.

Acid.	$p\mathrm{K}a$.
Formic	3·67
Acetic	4·73
Propionic	4·87
Butyric	4·83
Valeric	4·80
Capric	4·83
Oenanthic	4·88
Caprylic	4·84
Nonylic	4·96

With the exception of formic acid the constants vary between 4·7 and 5·0, and any tendency towards other values can hardly be discovered. One might expect a tendency towards higher values with increasing molecular weight, but evidently this lies within the experimental errors. Anyhow, it seems perfectly safe to assume that $p\mathrm{K}a$ of the higher acids is quite near 5·0.

According to what was said above we should expect, therefore, that fatty acids should show a marked change in their properties just around a $p\mathrm{H}$ of 5·0. As this is what Adam found them to do, it seems reasonable to assume that dissociation phenomena are the *cause* of the transition of the structure of films of fatty acids from close packed heads to close packed chains, to use Adam's nomenclature.

As to the question of *how* the transition takes place, it is easy to understand that the $-\mathrm{CO_2}$ groups would tend to give the molecules a lesser horizontal area than the $-\mathrm{CO_2H}$ groups. The former also are more symmetrical and have a greater affinity for water than the latter. If two layers are formed as according to Adam, it would be difficult to find any other explanation of this than that the fatty acid anions exist in two tautomeric forms, or that half of them remain in the undissociated form, even at a considerably higher $p\mathrm{H}$ than 5, owing to neighbour molecules.

It is probably very difficult to test experimentally the theory set out above. It might be done for other film-forming substances than fatty acids by comparing the $p\mathrm{H}$ of the transformation point with $p\mathrm{K}a$. The dissociation constants of these very substances are, however, as a rule not known, as they naturally are but very sparingly soluble. Another way might be to make measurements of the electric properties of the films according to Guyot and Frumkin.

If the electric moment per square unit of the film is not proportional to the number of molecules per square unit, but shows an irregularity around the critical pH (and probably a considerably higher value above than below that point), this fact would be in favour of our theory, but would not be in accordance with Adam's.

The theory, if correct, would supply a method for determining the dissociation constants of substances able to form monomolecular films. To get pKa, the negative logarithm of that constant, it is only necessary to fix the middle point of the pH-interval inside which the film changes its area. Even other properties of such films than the surface-tension may furnish similar determinations of the dissociation constants, since the change from the dissociated to the undissociated state must affect many other properties.

Summary.

A new theory is proposed, according to which the changes in the properties of monomolecular films with the acidity of the support are closely connected with the dissociation of the film-forming substances. The hydrogen ion concentration at which this change is most rapid is numerically equal to the negative logarithm of the acid dissociation constant of the substance.

It is pointed out that this relation may furnish a means of determining the dissociation constants of sparingly soluble substances.

Stockholm University,
April 1927.

LVIII. *On the Absorption of X-Rays and Multiple Ionization of Atoms.* *By* Lowell M. Alexander, *Ph.D.*, *Associate Professor of Physics, University of Cincinnati* *.

I. Introduction.

USING different methods of attack, A. H. Compton † and L. de Broglie ‡ have deduced similar theoretical expressions for the atomic fluorescent absorption coefficient τ_a, each equivalent to

$$\tau_a = [K_K Z^4 \lambda^3]^{\lambda < \lambda_K} + [K_L Z^4 \lambda^3]^{\lambda > \lambda_K} \quad . \quad . \quad . \quad (1)$$

* Communicated by the Author.

† A. H. Compton, Phys. Rev. xiv. p. 249 (1919).

‡ L. de Broglie, *Jour. de Phys. et Rad.* iii. p. 33 (1922); *C. R.* clxxiii. p. 1456 (1921).

where K_K and K_L are constants, Z the atomic number of the absorber, and λ the wave-length of the absorbed X-ray radiation.

On the experimental side, some investigators * find that equation (1) represents their experimental data with sufficient accuracy, while others † adopt fractional exponents instead of integers in equation (1).

The purposes of this article are to present:

(1) Absorption experiments by the author.
(2) A critical examination of published absorption-data.
(3) Proposed new laws of absorption.
(4) A discussion of multiple ionization of atoms.

Reference will be made to published data as shown:

B. = Barkla and White, Phil. Mag. xxxiv. p. 270 (1917).
H. = C. W. Hewlett, Phys. Rev. xvii. p. 284 (1921).
R. = F. K. Richtmyer, Phys. Rev. xviii. p. 13 (1921).
O.D.S. = Olson, Dershem, and Storch, Phys. Rev. xxi. p. 30 (1923).
R.W. = Richtmyer and Warburton, Phys. Rev. xxi. p. 721 A (1923).
A. = S. J. M. Allen, Phys. Rev. xxiv. p. 1 (1924), xxvii. p. 226 (1926), xxviii. p. 907 (1926).
Ar. = L. M. Alexander. This article.

II. Experimental Data.

Several investigators ‡ have remarked that as an absorption discontinuity is being approached on the short wave side, the rate of increase of absorption is considerably less rapid than at shorter wave-lengths. In order to investigate this phenomenon, the author has measured the absorption-coefficient of copper and aluminium over a range of wave-lengths 0·45 to 0·85 Å.

A molybdenum tube and a mechanical rectifier were used, together with Soller § collimators having an angular aperture of forty minutes of arc. The radiation was reflected from a

* E. A. Owen, Roy. Soc. Proc. xciv. p. 510 (1918). F. K. Richtmyer, Phys. Rev. xviii. p. 626 (1921).

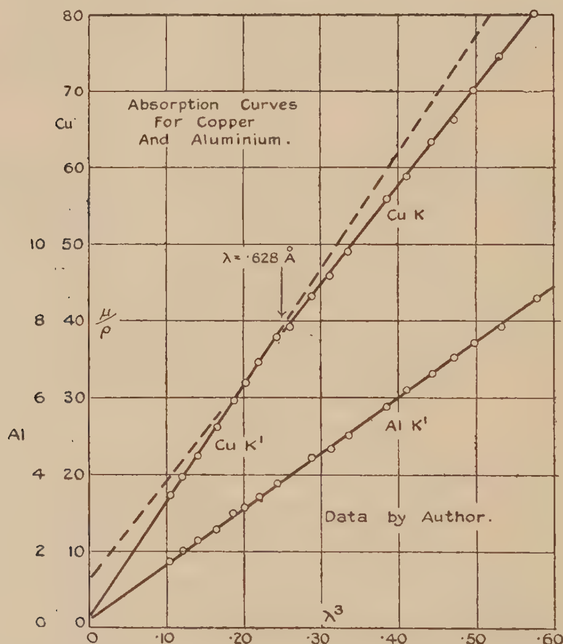
† Bragg and Peirce, Phil. Mag. xxviii. p. 626 (1914). Glocker, 'Atombau' (Engl. Trans.), Sommerfeld, p. 188. S. J. M. Allen, Phys. Rev. xxvii. p. 226 (1926).

‡ Stoner and Martin, Roy. Soc. Proc. cvii. p. 312 (1925). E. A. Owen, Roy. Soc. Proc. xciv. p. 510 (1918). F. K. Richtmyer, Phys. Rev. xviii. p. 13 (1921).

§ W. Soller, Phys. Rev. xxiv. p. 158 (1924).

calcite crystal. Methyl iodide was used in the ionization chamber. The same sheet of copper, or of aluminium, was used throughout the whole range, so that no error was introduced by the necessity of changing sheets during an experiment. These measurements were made in the first order of the spectrum, and the potential of the tube was kept sufficiently low that second-order radiation did not appear. This was determined directly by preliminary tests. Fig. 1 is a plot of the mass absorption-coefficient against the cube of the wave-length.

Fig. 1.



The data for aluminium, when plotted, represent accurately a single and continuous straight line over this range of wave-lengths. On the other hand, the data for copper lie accurately on two straight lines intersecting at 0·628 Å. This point of intersection I shall call the "KK′-break." The data of greater wave-length than the KK′-break comprise what I shall call K absorption, and those of shorter wave-length are termed K′ absorption. Thus, for copper, the law that the mass absorption-coefficient μ/ρ varies as the cube of the wave-length is accurately true within limited ranges of wave-length. If we pass from one of these ranges

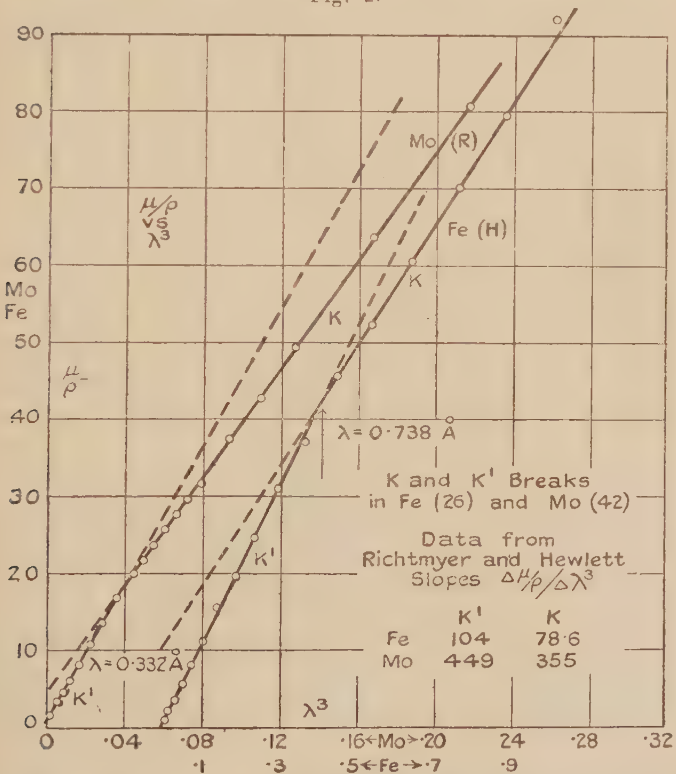
to another, a change in coefficient must be introduced in order to alter the slope of the line, and the slope for the K′ absorption is always steeper than that for the K absorption.

III. Data of other Investigators.

K *Absorption.*

In order to discover whether such a break in continuity KK′ occurs with other metals, the author replotted accurately the K-absorption data of those investigators who used homogeneous X-rays. The mass absorption-coefficient was

Fig. 2.



plotted against the cube of the wave-length from data taken unchanged from published results. In every case where the data extend over sufficient range of wave-lengths such a KK′-break was clearly shown. For brevity two examples are given here, these being selected from many others equally satisfactory. Fig. 2 shows the KK′-break for Mo (42), data

by Richtmyer, and for Fe (26), data by Hewlett. Wave-lengths at which these breaks occur are characteristic of the absorbing element.

TABLE I.

Data for KK′-break.

Element and Atomic No.	Observer.	Wave-length of KK′-break in Å units.	$\frac{\nu}{R}$	$\sqrt{\frac{\nu}{R}}$.
Fe 26	H.	·738	1235	35·1
Ni 28	A.	·695	1311	36·2
Cu 29...............	Ar.	·628	1451	38·1
	A.	·738	1235	35·1
	A.	·845	1078	32·8
Zn 30...............	A.	·531	1715	41·4
Mo 42	R.	·332	2745	52·4
Ag 47	A.	·272	3350	57·9
	R.	·277	3290	57·4
Sn 50	A.	·241	3781	61·5
W 74	A.	·113	8064	89·8
Pt 78	A.	·101	9022	95·0
Au 79...............	A.	·099	9214	96·0

Table I. gives the values of λ, $\frac{\nu}{R}$, and $\sqrt{\frac{\nu}{R}}$ for the KK′-break in various elements.

L *and* M *Absorption.*

When published L and M series absorption data are plotted as above, breaks similar to the KK′-breaks appear. However, the data for L and M series absorption data are too incomplete, and inaccurate, to permit of definite results, but such as could be found clearly indicate such a discontinuity in the slope of two straight-line branches. Furthermore, there is some evidence that more than one such break occurs in the L and M series absorption data.

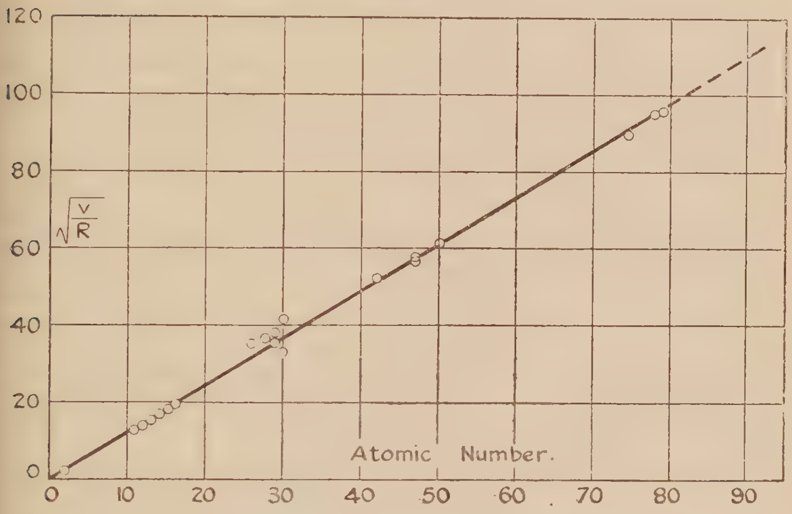
IV. Relation between Energy Level of KK′-breaks and the Atomic Number.

Fig. 3 shows $\sqrt{\frac{\nu}{R}}$ (see Table I.) at the KK′-break plotted against the atomic number of the absorbing element.

The best straight line through these points also passes through the zero point. The equation of this line, which specifies most nearly the frequency at the KK′-break for each element according to atomic number, is :—

$$\frac{\nu}{R} = 1{\cdot}5\, Z^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Fig. 3.



V. General Laws of Absorption.

Absorption data in the K and L regions are customarily represented by means of the equation,

$$\frac{\mu}{\rho} = k\lambda^3 + \frac{\sigma}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where k measures the slope of the line, and σ/ρ the value of μ/ρ for $\lambda = 0$, when μ/ρ is plotted as a function of λ^3.

The coefficients in equation (3) must be re-defined to agree with the results presented here.

$\left(\frac{\sigma}{\rho}\right)'_{\mathrm{K}}$ is here defined as the value of μ/ρ obtained by projecting the straight line representing K′ absorption to the μ/ρ axis. $\left(\frac{\sigma}{\rho}\right)_{\mathrm{K}}$ is here defined as the value of μ/ρ obtained by projecting the straight line representing K absorption to the μ/ρ axis. Similarly for the L region.

TABLE II.

μ/ρ Intercepts.

Absorber	1. $\left(\frac{\sigma}{\rho}\right)'_K$	2. $\left(\frac{\sigma}{\rho}\right)_K$	3. $\left(\frac{\sigma}{\rho}\right)'_L$	4. $\left(\frac{\sigma}{\rho}\right)_L$
H 1	·36			
Paraffin	·19			
C 6	·19			
O 8	·16			
Al 13	·20			
S 16	·25			
Fe 26	·22	10·0		
Ni 28	·80	—		
Cu 29	·54	6·0		
Zn 30	·52	2·4	1·0	
Mo 42	·50	4·2	3·0	
Ag 47	·41	2·6	2·0	27·0
Sn 50	–·42	2·8	0·0	12·0
Ba 56	·40	2·0	—	—
W 74	1·3	1·8	0·0	1·8
Pt 78	1·1	1·9	1·0	16·0
Au 79	1·0	1·7	0·9	—
Pb 82	—	—	0·01	21·0

Table II. shows the numerical values of these quantities for the various elements. k'_K is defined as the slope $\left(\frac{\mu}{\rho}\Big/\lambda^3\right)$ of the straight line representing K′ absorption. Similarly for k_K, k'_L, and k_L. Numerical values of these quantities for the various elements are shown in columns 3, 5, 7, and 9 of Table III.

Thus we may write in agreement with observed data :

$$\left.\begin{aligned}
\frac{\mu}{\rho} &= k'_K\lambda^3 + \left(\frac{\sigma}{\rho}\right)'_K \quad \text{for} \quad \lambda_{KK'} > \lambda > 0{\cdot}2\ \text{Å},^* \\
\frac{\mu}{\rho} &= k_K\lambda^3 + \left(\frac{\sigma}{\rho}\right)_K \quad \text{for} \quad \lambda_K > \lambda > \lambda_{KK'}, \\
\frac{\mu}{\rho} &= k'_L\lambda^3 + \left(\frac{\sigma}{\rho}\right)'_L \quad \text{for} \quad \lambda_{LL'} > \lambda > \lambda_K, \\
\frac{\mu}{\rho} &= k_L\lambda^3 + \left(\frac{\sigma}{\rho}\right)_L \quad \text{for} \quad ? > \lambda > \lambda_{LL'},
\end{aligned}\right\} \quad . \quad (4)$$

where λ_K is the wave-length at the K absorption limit and

* The data of those few investigators who have made measurements at wave-lengths less than 0·2 Å show consistent variations in the slope of the μ/ρ, λ^3 curves, as if two minute breaks occurred in this range. These breaks, however, occur at approximately the same wave-length for all absorbing elements, and are probably apparatus effects.

TABLE III.

1. Element.	2. Observer.	3. k'_K.	4. $C'_K \times 10^4$.	5. k_K.	6. $C_K \times 10^4$.	7. k'_L.	8. $C'_L \times 10^4$.	9. k_L.	10. $C_L \times 10$.
H 1	O.D.S.	0·272	[2740·]						
C 6	O.D.S.	0·995	[92·1]						
,,	H.	1·05	[97·3]						
,,	A.	1·45	134·2						
O 8	O.D.S.	2·78	[108·2]						
Al 13	A.	14·4	136·0						
,,	Ar.	14·6	138·0						
S 16	A.	27·7	135·6						
Fe 26	A.	100·0	122·3	—	—	—	—	10·5	12·8
,,	H.	104·0	127·0	78·6	96·2				
,,	R.W.	110·0	134·6						
Co 27	R.W.	124·0	137·7						
Ni 28	A.	135·5	129·5	106·2	101·4	—	—	12·6	12·1
,,	R.W.	144·0	137·3						
Cu 29	B.	152·1	137·0						
,,	A.	151·0	135·8	119·0	107·0	—	—	14·0	12·6
,,	Ar.	152·0	136·8	128·8	115·8				
,,	R.W.	153·0	136·0						
Zn 30	A.	166·7	134·4	125·5	101·2	—	—	16·5	13·3
,,	A.	172·8	139·3	162·0	[130·6]				
Mo 42	R.	449·0	138·5	355·0	109·5	56·1	17·3	48·3	14·9
Ag 47	A.	670·0	147·5	555·0	122·5	74·1	16·3	55·8	12·3
,,	R.	674·0	148·5	552·0	121·5	93·0	20·5		
Sn 50	A.	750·0	142·8	583·0	111·0	97·0	18·5	59·6	11·3
Ba 56	A.	883·0	123·4	682·0	95·2	137·0	19·1		
W 74	A.	2080·0	128·0	1812·0	111·3	310·0	19·0		
Pt 78	A.	2704·0	142·5	1941·0	102·3	351·0	18·5	290·0	15·2
Au 79	A.	2620·0	132·8	1875·0	97·0				
Pb 82	R.	—	—	—	—	523·0	23·9	312·0	14·3
,,	A.	—	—	—	—	471·0	21·6	357·0	16·4
Th 90	A.	—	—	—	—	527·0	18·6		
	Average		136·0		107·0		19·3		13·5

$\lambda_{KK'}$ is the wave-length at the KK′-break. k and σ/ρ are to be taken from Tables II. and III. These expressions are accurate to 1 per cent. approximately, while the ordinary cube law is in error by 30 per cent. at some wave-lengths.

Both theoretical and experimental results indicate that the fluorescent mass absorption-coefficient τ/ρ is also a function of the atomic number Z and the atomic weight A of the absorbing element. Thus the complete expression, as usually given, is

$$\frac{\tau}{\rho}=\frac{CZ^4\lambda^3}{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C is a constant for different materials, but assumes different values for the K, L, M absorptions in the same metal. In accordance with the results presented here, C assumes the values :

$$\left.\begin{array}{llll} C_i = C'_K & \text{for} & \lambda_{KK'} > \lambda > 0{\cdot}2\ \text{Å}, \\ C_i = C_K & \text{for} & \lambda_K > \lambda > \lambda_{KK'}, \\ C_i = C'_L & \text{for} & \lambda_{LL'} > \lambda > \lambda_K, \\ C_i = C_L & \text{for} & \ ? > \lambda > \lambda_{LL'} . \end{array}\right\} \quad . \quad . \quad . \quad (6)$$

If k_i represents the slope of any of the straight lines obtained experimentally by plotting μ/ρ against λ^3, the corresponding C_i is computed from the equation,

$$C_i=\frac{k_iA}{Z^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Columns 4, 6, 8, and 10 of Table III. show the numerical values of the C's computed from equation (7). It is seen that these values are approximately constant for any given portion of the absorption data. More numerous and, probably, more accurate data are necessary before it can be decided whether C_i is a true constant.

If the C's be assumed constant for all elements, and the mean value be used, a less accurate but more general formulation of absorption data is given by the equation,

$$\frac{\mu}{\rho}=\frac{C_iZ^4\lambda^3}{A}+\frac{\sigma}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\begin{aligned} C'_K &= 136 \times 10^{-4}, \\ C_K &= 107 \times 10^{-4}, \\ C'_L &= 19{\cdot}3 \times 10^{-4}, \\ C_L &= 13{\cdot}5 \times 10^{-4}. \end{aligned}$$

The values for σ/ρ are to be taken from Table II.

The mass absorption-coefficient μ/ρ may be expressed as atomic absorption coefficient μ_a by the use of the relation,

$$\mu_a = \frac{A}{n}\frac{\mu}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where A is the atomic weight and n is Avagadro's number. Thus

$$\mu_a = C_j Z^4 \lambda^3 + \sigma_a, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where

$$(C_a)'_K = 2{\cdot}24 \times 10^{-26},$$

$$(C_a)_K = 1{\cdot}77 \times 10^{-26},$$

$$(C_a)'_L = 0{\cdot}318 \times 10^{-26},$$

$$(C_a)_L = 0{\cdot}223 \times 10^{-26},$$

$$\sigma_a = \frac{\sigma}{\rho}\frac{A}{n}.$$

VI. Multiple Ionization.

The sudden change in the slope of the absorption curve which occurs at the KK′-break, the wave-length of which is characteristic of the absorbing element, must represent some energy change in the atom. The only explanation which seems reasonable is that the KK′-break is the point at which double K ionization sets in From this viewpoint the frequency of the KK′-break marks the point where the quantum of impinging radiation has just sufficient energy to remove the two K electrons as a single act.

The wave-length just at the short-wave side of the K absorption limit marks the point where the quantum of impinging radiation has just sufficient energy to remove the first K electron. The photo-electron under these conditions would have zero velocity at the periphery of the atom. As the frequency of the radiation is increased, the probability of absorption decreases, as is shown by the downward trend of the absorption curve. Also, if the energy of the quantum is entirely transferred to the electron, the speed of the photo-electron should increase regularly with the frequency until the quantum has just sufficient energy to remove both K electrons as a single act. At this point twice as many electrons should be produced, although their speed at the periphery of the atom is again zero. It is not unreasonable to suppose that at higher frequencies the probability of

absorption is decreased slightly, as shown by the increased slope of the μ/ρ, λ^3 curve at frequencies higher than that of the KK′-break.

Although the references to double K ionization are for elements of small atomic number where the KK′-break would be difficult to observe, and are disappointingly meagre, yet comparisons may be made between these values and what is here interpreted as double K ionization. I therefore note all such references as are known to me :—

(1) The electron impact measurement of the double K ionization potential of helium (79·5 volts) measured by Franck and Knipping*.

(2) The discovery by Hjalmar of the so-called "spark lines" in the X-ray spectra. Wentzel† attributed these lines to multiple ionization effects.

(3) L. A. Turner‡, using the data of Hjalmar, has computed with certain assumptions the double K ionization energy levels for elements from atomic numbers 11 to 16.

Equation (2) of this article predicts the double K ionization potential of helium to be 81·3 volts as compared with the observed value of 79·5. Franck and Knipping's value for helium and Turner's values for atomic numbers 11 to 16 are plotted in fig. 3.

Table IV. column 4 shows the ratio of ν/R for the KK′-break, computed from equation (2), to the value of ν/R for the K limit in a few elements. According to the ideas presented here, this is the ratio of the energy necessary for the removal of both K electrons as a single act to the energy necessary for the removal of the first K electron. It is usually stated that slightly more than twice as much energy is required for double than for single K ionization. It is certain that this is not true for helium, as the ratio is known to be 3·24. It is seen that the ratio as here computed varies from 3·31 for helium to 1·5 for uranium.

Table IV. column 5 shows the values of ν/R necessary for double K ionization. The experimental value for helium was observed by Franck and Knipping. The other values were computed by Turner. Column 6 shows the ratio of

* Frank and Knipping, *Phys. Zeit.* xx. p. 481 (1919).

† G. Wentzel, *Ann. der Physik*, lxvi. p. 437 (1921), lxxiii. p. 647 (1924).

‡ L. A. Turner, Phys. Rev. xxvi. p. 143 (1925).

column 5 to column 3. It is seen that the observed ratio for helium (3·24) compares favourably with the computed

TABLE IV.

1. Atomic Number.	2. ν/R for KK′-break (eq. 2).	3. ν/R for K limit.	4. Ratio $\frac{(\nu/R)_{KK'}}{(\nu/R)_K}$.	5. ν/R for double K ionization.	6. Ratio.
2	6·0	1·81	3·31	5·86	3·24
11	181·5	79·04	2·30	159·64	2·02
12	216·0	96·00	2·25	194·06	2·02
13	253·5	114·88	2·21	232·09	2·02
14	294·0	135·6	2·17	273·59	2·02
15	337·5	157·3	2·14	318·94	2·03
16	384·0	182·0	2·11	367·74	2·02
20	600·0	297·4	2·02		
30	1350·0	712·0	1·90		
40	2400·0	1326·0	1·81		
50	3750·0	2149·0	1·74		
60	5400·0	3211·0	1·68		
70	7350·0	4522·0	1·62		
80	9600·0	6113·0	1·57		
90	12150·0	8062·0	1·51		
92	12696·0	8477·0	1·50		

ratio (3·31). However, Turner's computed values give a constant ratio (2·02) for elements of atomic number 11 to 16, whereas column 4 shows a decrease in this ratio as the atomic number increases. Turner computed his multiple ionization terms by making the assumption that the energy of removal of an L electron depends only upon $Z-x$, where x is the number of K electrons present. It is difficult to justify this assumption, except as a first approximation.

The author desires to express his appreciation to Professors L. T. More and R. C. Gowdy for their keen interest and many helpful suggestions in the course of this work.

Cincinnati, Ohio,
August 1, 1926.

LIX. *Some Interference Effects in the Near Infra-red.*

By A. M. TAYLOR *and* E. K. RIDEAL *.

WHEN examining thin films of crystalline substances in the infra-red spectrum it is usually assumed that the logarithm of the ratio between the intensities of a beam of radiation of a very narrow range of frequencies, before and after transmission through the crystal slice, is a measure of the absorption coefficient for the particular frequency range employed. Some effects to be described show, however, that this ratio of transmitted to incident intensity may be modified by interference phenomena.

A consideration of the intensity I_t of the transmitted beam will lead to the expression

$$I_t = I_0(1-R_1)(1-R_2)e^{-\alpha z}, \quad . \quad . \quad . \quad . \quad (1)$$

where $\alpha = \dfrac{4\pi n\nu K}{c}$. In this expression z is the thickness of the crystal slice, n the refractive index for the particular frequency ν, c the velocity of light in free space, and K is an extinction coefficient such that when $4\pi K$ is unity the intensity of the light is reduced to $\dfrac{1}{e}$ in travelling through one wave-length in the crystal. R_1 and R_2 are the reflexion coefficients at the front and back surfaces of the crystal plate respectively, and

$$R_1 = R_2 = \frac{(n-1)^2+n^2K^2}{(n+1)^2+n^2K^2}.$$

Havelock [1] has examined the behaviour of R and has shown that K has very little effect in altering the frequency at which R becomes a maximum.

If for a first approximation R_1 and R_2 be put equal to $\dfrac{(n-1)^2}{(n+1)^2}$, (1) becomes

$$\frac{I_t}{I_0} = \frac{16n^2}{(n+1)^4}e^{-\alpha z}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The usual method of procedure is to plot the experimental values of I_t/I_0 against λ the wave-length of the radiation, and a curve is obtained having one or more minima. These minima correspond with maximum values of α but do not necessarily coincide with them, for on differentiation of (2)

* Communicated by Prof. Alfred W. Porter, F.R.S.

with respect to λ,

$$\frac{d}{d\lambda}\left(\frac{\mathrm{I}_t}{\mathrm{I}_0}\right) = \left\{\left[\frac{32n(1-n)}{(1+n)^5}\cdot\frac{dn}{d\lambda}\right] - z\left[\frac{16n^2}{(1+n)^4}\,\frac{d\alpha}{d\lambda}\right]\right\} e^{-\alpha z},$$

and the minima must be given by the equation

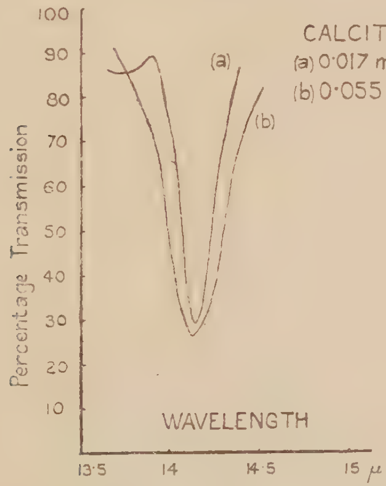
$$\frac{d}{d\lambda}\left(\frac{\mathrm{I}_t}{\mathrm{I}_0}\right) = 0$$

or

$$\frac{d\alpha}{d\lambda} = \frac{1}{z}\cdot\frac{2(1-n)}{n(1+n)}\cdot\frac{dn}{d\lambda}, \quad \ldots \ldots \quad (3)$$

whereas the maxima of α are given by $\frac{d\alpha}{d\lambda} = 0$ in the expression for α as a function of λ, when reflexion losses are neglected. For z large the coincidence will be almost exact, but for small values of z the discrepancy may become considerable, especially as $\frac{dn}{d\lambda}$ is large in the neighbourhood of an absorption band.

Fig. 1.



In the examination of the absorption spectrum of the crystalline carbonates Schaefer [2] and others have made use of very thin specimens for determining the bottom of deep bands. Clearly the thinness of the slice may introduce a correction in the value found for the apparent characteristic frequency. The authors have examined calcite cut perpendicularly to the optic axis, at $14\,\mu$, and have found such a shifting of the minimum with thin specimens as expression (3) predicts. Fig. 1 shows the curves obtained for two

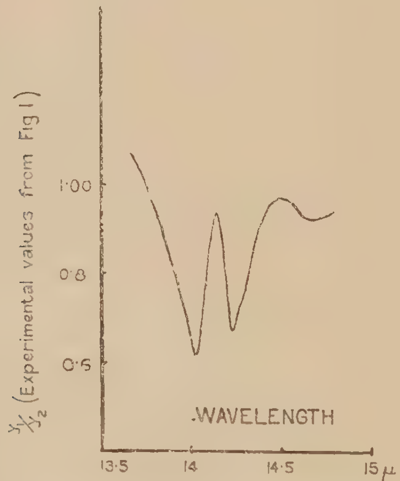
pieces of calcite—(*a*) 0·017 mm. thick, and (*b*) 0·055 mm. thick. (*a*) has a minimum at 14·135 μ, whereas that of (*b*) occurs at 14·125 μ. The minimum is shifted in the thinner specimen towards the reflexion maximum found by Schaefer [3] at 14·16 μ.

This is not the complete account of the effect however, for if $y = \frac{I_t}{I_0}$ at any particular wave-length, then if two different crystals of thickness z_1 and z_2 be examined, from equation (1)

$$\frac{y_1}{y_2} = e^{+\alpha(z_2 - z_1)},$$

so that if y_1/y_2 be plotted against λ a curve will be obtained from which reflexion losses are absent and a minimum of

Fig. 2.



y_1/y_2 should coincide exactly with a maximum of α. Fig. 2 shows the result of plotting the experimental values in this manner, and indicates by the presence of several maxima and minima the superposition of the interference effects to which we have alluded.

A complete examination of the effects of interference would involve a series of beams arising from successive reflexions, but it will be sufficient for this purpose to consider only the first two terms, since all after the first two will be negligible owing to absorption in the crystal.

If the intensity of a beam falling upon the crystal slice at

normal incidence be I_0, and if the emergent beam consists of two parts I_1 and a twice reflected portion I_2, consideration of the path of the beams will show that

$$I_1 = I_0(1-R_1)(1-R_2)\,e^{-\alpha z} \quad . \quad . \quad . \quad . \quad (4)$$

and

$$I_2 = I_0(1-R_1)(1-R_2)R_2^2\,e^{-3\alpha z}, \quad . \quad . \quad (5)$$

or

$$\frac{I_2}{I_1} = R_2^2\,e^{-2\alpha z}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Putting $R_2 = R_1$, then from (4) and (6)

$$\frac{I_2}{I_1} = \frac{R_2}{(1-R)^4}\left(\frac{I_1}{I_0}\right)^2, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and writing the right-hand side of this equation equal to G^2, since the amplitude of vibration is proportional to the square root of the intensity, then $\frac{A_2}{A_1} = G$. The amplitude A_t of the transmitted beam is of two parts A_1 and A_2, so that

$$A_t^2 = A_1^2 + A_2^2 + 2A_1A_2\cos\phi,$$

where ϕ is the phase angle. Hence the transmitted intensity must be given by

$$I_t = I_1(1+G^2+2G\cos\phi), \quad . \quad . \quad . \quad . \quad (8)$$

and finally using equ. (4)

$$\frac{I_t}{I_0} = (1-R_1)(1-R_2)(1+G^2+2G\cos\phi)\,e^{-\alpha z}. \quad . \quad (9)$$

As before, if $y = \frac{I_t}{I_0}$ and two different thicknesses z_1 and z_2 be used,

$$\frac{y_1}{y_2} = e^{-\alpha(z_2-z_1)}\cdot\frac{(1+G_1^2+2G_1\cos\phi_1)}{(1+G_2^2+2G_2\cos\phi_2)}. \quad . \quad . \quad (10)$$

The angle ϕ is given by the relation

$$\phi = \frac{4\pi nz}{\lambda},$$

since the path difference between the interfering rays is $2nz$ for normal incidence.

Equation (7) shows that G is small, and hence from (8) I_t and I_1 cannot differ by very large amounts; an estimate of G may be made from (7) by writing I_t for I_1, whence

$$G = \frac{I_t}{I_0}\,\frac{R}{(1-R)^2}.$$

For calcite Schaefer and Schubert[3] find R about 10 per cent. at a point where I_t/I_0 is about 70 per cent. for a slice 0·07 mm. thick, and from this

$$G = 0\cdot 9.$$

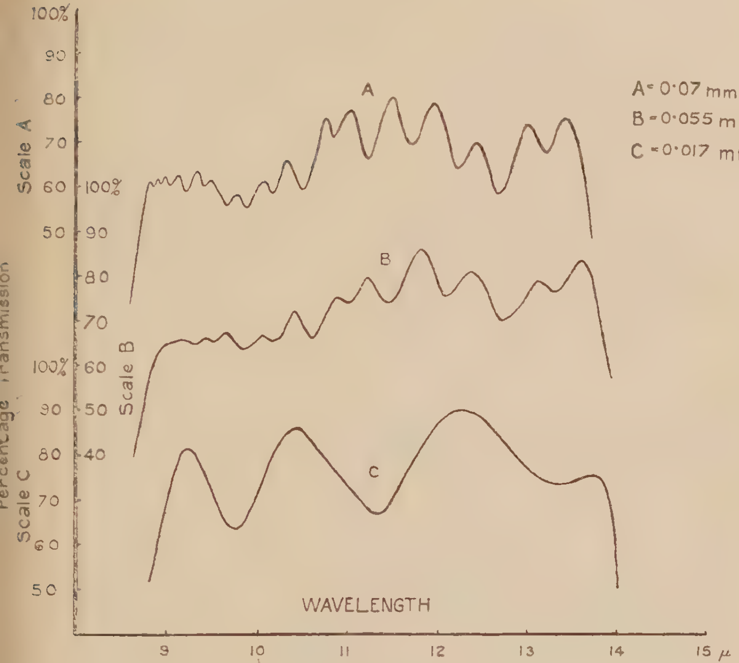
This value of G is sufficiently large to cause a pronounced variation in y_1/y_2 as given by expression (10), and the peculiar curve shown in fig. 2 is fully explained as due to interference between the rays concerned.

Far removed from an absorption band α is zero, and equ. (9) shows that interference should be indicated by variations in I_t/I_0. Such variations are found in the absorption spectrum of calcite and other carbonates[2], in regions where there can be no vibration frequencies characteristic of the material. If these ripples are due simply to interference the difference between the wave numbers of successive minima should be equal to a constant divided by the refractive index,

$$\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right) = \frac{1}{2nz}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

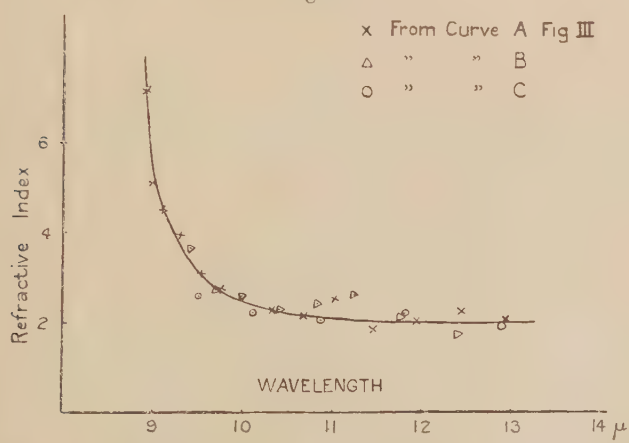
where n is the mean refractive index between λ_2 and λ_1. To test this the authors have examined two different thicknesses of calcite cut perpendicularly to the optic axis, and the results are plotted in fig. 3 together with those of Professor Schaefer's examination of a thicker specimen. The character of the ripples obtained in each case shows at once that they are due purely to interference, and a number of bands hitherto attributed to combination terms may be explained in this manner. The refractive index of calcite parallel to the optic axis may be calculated from (11), and the values found from the three sets of measurements are plotted in fig. 4. The results obtained from the three different crystals agree excellently together. The rapid rise of refractive index on the long-wave length side of the fundamental frequency at 7·0 μ is particularly noticeable, and is to be expected from the accepted theory of dispersion. The experimental points lie above the curve in the region 11 μ to 11·4 μ for the reason that the incident beam consisted of a cone of rays of which the axis was parallel to the optic axis of the crystal, so that the extreme rays had a component vibration in the direction of the axis. They were then subject to the influence of the fundamental frequency of the CO_3 group at 11·3 μ[3], of which the electric vector is along the axis[4] and in consequence experienced an increased refractive index in this neighbourhood. The refractive

Fig. 3.



Transmission of Calcite, slice cut ⊥ to optic axis.

Fig. 4.



index for the ordinary ray is, however, not subject to this increase, and therefore the curve in fig. 4 is drawn so as to neglect these high values.

The apparatus used was that described in a previous paper [5]. Our thanks are due to Professor Schaefer, now of Breslau, who kindly provided the figures of his measurements on calcite of 0·07 mm. thickness.

Laboratory of Physical Chemistry,
Cambridge.

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1. Havelock, Proc. Roy. Soc. A, cv. p. 488 (1924).
2. Schaefer, Bormuth & Matossi, *Zeit. für Phys.* xxxix. p. 648 (1926).
3. Schaefer & Schubert, *Ann. der Phys.* l. p. 283 (1916).
4. Kornfeld, *Zeit. für Phys.* xxvi. p. 205 (1924).
5. Rawlins, Taylor & Rideal, *Zeit. für Phys.* xxxix. p. 660 (1926).

LX. *The Crystal Structure of some of the Alums.* By J. M. Cork, *Ph.D., Assistant Professor of Physics, Michigan University, U.S.A.* *

[Plate XVI.]

Introduction.—The alums make an interesting group of crystals for X-ray analysis. Although the molecule is rather complicated, there are so many isomorphous members in the group, differing from one another simply by the replacement of a single atom, that the solution of the structure is not hopeless, especially regarding the positions of the heavier atoms. They possess the symbolic chemical formula

$$A\,.\,B\,.\,(SO_4)_2\,.\,12H_2O,$$

in which A represents a monovalent metallic ion, B a trivalent metallic ion, and S, generally sulphur, may be replaced by selenium or tellurium. B is commonly aluminium, chromium or iron; while A may be ammonium, potassium, rubidium, cæsium or thallium. All of the alums examined form very perfect crystals of octahedral shape. Crystallographic considerations assign them to the pyritohedral class of the cubic system.

Vegard and Schjelderup † on the basis of spectrometer measurements assigned positions to the atoms in the unit cell so as to make observed and calculated intensities agree. This assignment was made without regard to the space group and led to a complicated and improbable

* Communicated by Professor W. L. Bragg, F.R.S.
† *Annalen d. Physik,* liv. p. 146 (1917).

arrangement. P. Niggli *, using the data of Vegard and Schjelderup, assigned the alums to the space group T_h^2 and suggested possible arrangements. R. W. G. Wyckoff †, by means of Laue and rotation photographs, concluded that the correct assignment of the space group was T_h^6 rather than T_h^2.

In the present paper new intensity measurements have been made by the X-ray spectrometer upon all orders of the three principal plane sets, (111), (110), and (100), for ammonium, potassium, rubidium, cæsium, and thallium-aluminium alums and potassium chrome alum. The dimensions of the unit cell have been accurately determined in each case. In addition, rotation photographs have been taken to verify the space group assignment. Using the method of Fourier analysis, as simplified by Duane, and used so successfully in the case of many relatively simple structures, an attempt has been made to locate the position of some of the heavier atoms in this more complicated structure. In addition, use is made of the atomic structure factor curves to check the agreement between calculated and experimental F values, particularly in the case of high order reflexions, where the effect of the lighter atoms may be neglected. This, together with consideration of the atomic domain, or dimensions required for the particular atoms or groups of atoms in other structures, and the symmetry of space group, limits very markedly the number of possible arrangements.

Lattice Constants.—Four molecules are ascribed to the unit cubic cell. The eight metal atoms take positions at the corners, centre, centre of faces and mid-points of edges of the cell, making a rock-salt arrangement of monovalent and trivalent metals. The lengths of the cube edges obtained are tabulated in Table I. Use was made of as many orders as

Table I.

Edge of Unit Cubic Cell for various Alums.

Alum.	Edge of unit cell.
$NH_4Al(SO_4)_2 . 12H_2O$............	12·18 Å.
$K . Al . (SO_4)_2 . 12H_2O$	12·14 „
$K . Cr . (SO_4)_2 . 12H_2O$	12·14 „
$Rb . Al . (SO_4)_2 . 12H_2O$	12·20 „
$Cs . Al . (SO_4)_2 . 12H_2O$	12·31 „
$Th . Al . (SO_4)_2 . 12H_2O$	12·21 „

* *Phys. Zeits.* xix. p. 225 (1918).
† Amer. Journ. of Sci. v. p. 209 (1923).

possible in each plane set. A slight increase in dimensions is observed as potassium is replaced by rubidium and cæsium in turn. Thallium appears to occupy about the same space as rubidium, while the ammonium ion requires only slightly less room. Chromium appears to replace aluminium with a very slight, if any, change in dimensions.

Spectrometric Intensity results.—Intensity measurements were made using a Bragg ionization spectrometer equipped with string electrometer and potentiometer as previously* described. Each integrated reflexion was compared with that from the (400) plane of rocksalt whose value was taken as 100×10^{-6}. Table II. summarizes the data obtained. The reflecting plane is listed in column 1 and the approximate value of the sine of the reflecting angle in column 2, since this varied slightly with the different alums, while columns 3, 5, 7, 9, 11, and 13 contain the experimental values of the integrated reflexions ρ for each alum.

For the case of the ideal mosaic crystal Darwin † has developed a relationship involving the integrated reflexion $\frac{Ew}{I}$, or ρ, and the structure factor F, which may be approximated as follows :—

$$\rho = F^2 \cdot \frac{n^2\lambda^3 e^4}{4m^2c^4} \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot \frac{1}{\mu+\alpha\rho} \cdot e^{-B\sin^2\theta}.$$

In this formula n represents the number of unit cells per cubic centimetre, λ and c the wave-length and velocity of X-rays, e and m the charge and mass of the electron respectively, θ the glancing angle of incidence for X-ray reflexion, α, a constant for a particular crystal specimen, being an indication of the perfection of the crystal, so that $\alpha\rho$ represents the effective increment to the absorption coefficient due to extinction, μ is the linear absorption coefficient, and $e^{-B\sin^2\theta}$ a temperature factor due to the heat motion of the atoms.

If, as an approximation, α be assumed zero and the temperature factor be taken as unity, then for each value of ρ, a value of the structure factor F may be obtained. The value of the absorption coefficient for ammonium alum was measured experimentally using several thicknesses of the absorber, and that of the other alums found by

* R. W. James, Phil. Mag. xlix. p. 585 (1925).

† Phil. Mag. xxvii. pp. 315, 675 (1915); xliii. p. 800 (1922).

TABLE II.—Intensity of Reflexion and Structure Factor for the various Alums.

Plane.	Sin θ.	$NH_4Al(S_4O)_2 . 12H_2O$.		$KAl(SO_4)_2 . 12H_2O$.		$KCr(SO_4)_2 . 12H_2O$.		$Rb . Al . (SO_4)_2 . 12H_2O$.		$Cs . Al . (SO_4)_2 . 12H_2O$.		$Tl . Al . (SO_4)_2 . 12H_2O$.	
		$\rho\times10^6$.	F.	$\rho\times10^6$.	F.	$\rho\times10^6$.	F.	$\rho\times10^6$.	F.	$\rho\times10^6$.	F.	$\rho\times10^6$.	F.
111	·0494	70·0	86	8·8	38	21·0	78	1·11	29	17·2	101	6·5	113
200	·0578	13·9	42	·8	13	1·6	22	2·11	43	16·0	107	3·36	89
220	·0822	76·3	116	78·8	142	67·2	174	26·2	180	49 0	221	29·2	308
222	·0996	—	—	1·15	19	3·9	47	4·15	79	31·0	192	9·7	195
400	·1161	63·5	125	56·6	15	44·3	170	31·2	233	51·8	268	19·1	295
333	·1492	36·8	111	30·5	125	11·7	102	10·8	158	29·0	231	9·0	236
440	·1645	1·04	19	6·9	62	8·7	90	3·18	90	13·2	164	5 2	186
600	·1909	39·1	129	36·4	154	30·0	174	16·7	223	40·1	310	10·2	283
444	·1982	1·37	25	·05	6	1·45	41	·95	55	5·4	116	1·9	125
800	·2317	·07	6	·33	16	—	—	·59	47	4·05	110	1·48	121
660	·2467	11·5	80	15·6	116	15·4	169	5·52	147	17·4	234	5·05	228
555	·2481	1·0	24	2·68	49	—	—	·99	64	2·9	96	1·6	131
10.00	·2716	3·7	48	5·1	71	3·3	77	1·81	90	·74	51	1·67	135
666	·2977	10·3	86	6·6	86	4·9	96	2·5	122	11·8	217	2·05	164
880	·3289	3·34	52	5·02	79	3·6	88	1·8	101	4·3	140	1·75	162
12·00	·3475	·08	8	—	—	—	—	·47	90	4·1	143	·29	69
777	·3475	3·07	53	·84	34	·46	33	—	—	·94	68	·02	18
888	·3971	—	—	·15	16	·09	16	·06	22	1·1	81	·16	56
14.00	·4057	·18	14	·32	23	—	—	·19	38	·89	74	·16	57
10.10.0	·4112	·25	17	·63	33	·72	52	·08	25	·47	54	·18	61
999	·4470	·50	25	—	—	—	—	—	—	·45	56	·02	25
16.00	·4638	·60	28	·59	35	—	—	·48	67	·46	59	·13	56
12.12.0	·4945	·23	18	·47	32	·63	55	·13	36	·47	61	·11	54
10.10.10	·4967	1·06	39	—	—	—	—	—	—	·08	26	—	—

computation from this, making use of the data of Windgardth * on atomic absorption coefficients. These values of F are tabulated in columns 4, 6, 8, 10, 12, and 14.

Space Group.—Fig. 1 (Pl. XVI.) shows a rotation photograph taken from cæsium alum, using the (100) plane, set with the c axis parallel to the axis of rotation. Similar photographs were taken for the other alums. To distinguish between questionable planes the spectrometer was used. The abnormal spacing characteristic of the space group T_h^6 is, that for planes of indices $\{hko\}$ the spacing is halved if h is odd, for $\{okl\}$ if k is odd, for $\{hol\}$ if l is odd. No reflexions were found contrary to this requirement, thus confirming the assignment of Wyckoff.

There are thus 24 generally equivalent positions. The eight sulphur atoms in each cell must be distributed, one in each small cell, on the trigonal axis. They therefore introduce only one parameter. The sulphate oxygens being 32 in number must be of two kinds, as would be expected if the SO_4 group maintained the tetrahedral form usually assigned it. Eight of the oxygen atoms would thus be arranged similarly to the sulphur atoms, while the remaining 24 would occupy the general positions, introducing in all four more parameters. If the sulphate group, however, maintains in the alums the form it appears to possess in other structures, these 24 atoms would give 3 to each small cell, arranged about the 3-fold axis, forming with the oxygen atom on the axis an equilateral tetrahedron whose base is perpendicular to the 3-fold axis. The oxygen atoms having a diameter of about 2·7 ångströms are thus in close packing array having the sulphur at the centre of mass of the tetrahedron, the sulphur atom being so small that it can well be accommodated by the space before the four oxygens. Thus, if the position of the relatively heavy sulphur atom can be obtained, and the orientation of the tetrahedron along the diagonal, then only the angular position of the tetrahedron thought of as rotating about the 3-fold axis is left undetermined. Similarly the 48 oxygen atoms of the water may be considered as two groups of 24 each in generally equivalent positions. Having located the SO_4 tetrahedron and considering the dimensions of the monovalent and trivalent metal atoms, only certain available space remains for the other oxygen planes normal to the trigonal axes. The 96 hydrogen atoms making 4 sets of 24, occupying generally equivalent

* *Zeit. f. Physik*, viii. p. 363 (1922).

positions, can scarcely be considered, as their scattering power is so small. The space occupied by them must be small. However, in the hexagonal close-packed assemblage of oxygen atoms only 13·94 cubic centimetres per atom is required, whereas in the alum structure, treating the monovalent metal atom as an oxygen atom, about 21·7 cubic centimetres per atom is allowed, so that considerable space is left for the hydrogen atoms, if necessary.

Fourier Analysis of Electron Distribution.—If a set of crystal planes be considered, the distribution of diffracting centres (electrons) in sheets parallel to the planes is a periodic function of the spacing of the plane set and may be expressed by a Fourier series. It has been shown * that the first order amplitude of reflexion from this plane set depends upon the first coefficient of the Fourier series, the second order upon the second coefficient, etc. Conversely, if the amplitude of reflexion of a number of orders for any plane set is known, then it becomes possible to obtain the electron distribution in sheets parallel to the plane. The method has been considerably simplified † and employed in the case of several simple crystals ‡. In the form developed by A. H. Compton the sheet electron density P_z for the unit cell at a distance z along a direction perpendicular to the plane set giving the information is given by the series

$$P_z = \frac{Z}{d} + \frac{2}{d}\left(F_1 \cos\frac{2\pi z}{d} + F_2 \cos\frac{4\pi z}{d} + \ldots + F_n \cos\frac{2\pi n z}{d}\right),$$

where Z denotes the number of electrons in the unit cell and F_n is the structure factor for the nth-order reflexion from the plane set being considered, and d is the spacing of the planes in the direction considered. By dividing by the number of molecules in the unit cell, the electron distribution within the molecule is given.

The value of F given in Table II., being the square root of a quantity, may be either positive or negative in sign. In this series of alums, however, the correct sign is readily observed, as the origin is taken as the centre of a monovalent metal atom, and when this is replaced by a heavier atom F should increase algebraically. If F decreases

* W. H. Bragg, Phil. Trans. Roy. Soc. A, ccxv. p. 253 (1915).

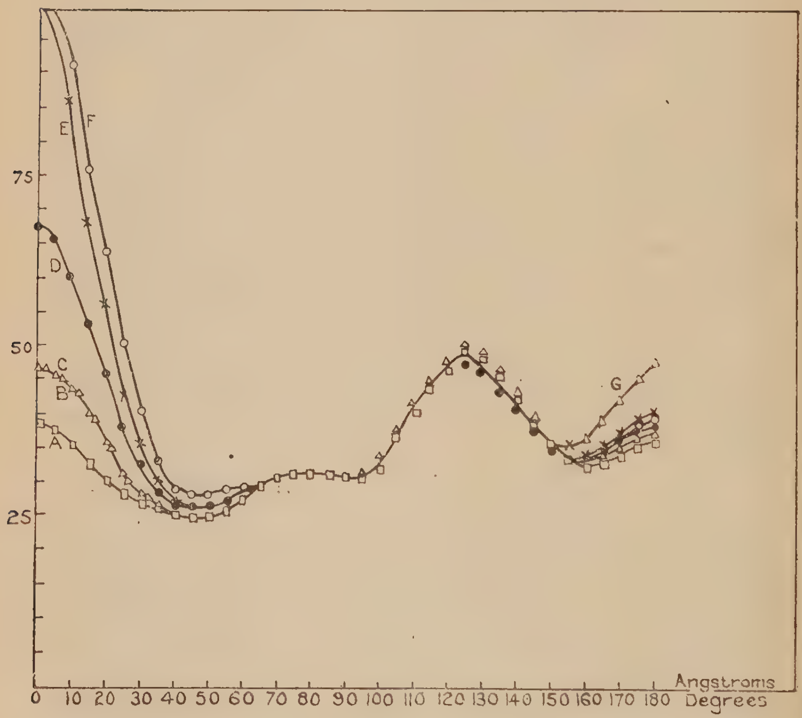
† W. Duane, Proc. Nat. Acad. Sci. xi. p. 489 (1925). A. H. Compton, 'Theory of Electrons,' p. 154.

‡ R. J. Havighurst, Proc. Nat. Acad. Sci. xi. p. 502 (1925) *et seq.* J. A. Bearden, Phys. Rev. vol. xxix. p. 20 (1927). W. L. Bragg and J. West, Proc. Roy. Soc. cxi. p. 691 (1926).

numerically when the heavier metal atom is substituted, then it must be negative in sign. For example, for potassium-aluminium alum F_{111} and F_{777} are considered negative. In order to make the series more rapidly convergent, the F values were multiplied by a factor of the form of the Debye temperature factor.

Fig. 2.

Electron Distribution in Planes parallel to the (111) set.



The values of P_z for planes normal to the (111) set for the different alums, computed at intervals of 0·1 ångströms, are shown in fig. 2. This plane set gives alternately layers of monovalent and trivalent metals. Thus if the distance from one monovalent metal layer to the next adjacent similar layer be taken as 360° or 7·06 ångströms for the alums, then the trivalent metal layer will lie at 180° or 3·53 ångströms, and if the sulphur atoms were each at the centres of the small cubes they would lie at 90° or 1·76 ångströms. If, however, the sulphur is displaced

along the diagonal of the small cube any number of degrees, then there will appear sulphur planes of two types. That is, if we imagine a shift of the sulphur of ϕ degrees toward the aluminium, then for a single molecule of alum one plane of $\frac{3}{4}$ atom of sulphur will occur at $90° + \phi$ and another plane of $\frac{1}{4}$ atom at $90° - 3\phi$, and symmetrical positions.

The remarkable similarity of the curves for the different alums indicates clearly the effect of changing either the monovalent or trivalent metal atom. At 0° occurs the electron density on the plane through the centres of monovalent metal atoms. Since number of electrons is represented in the figure by areas, the difference between any two of these curves should give the difference in the number of electrons in the corresponding atoms. Thus the potassium-aluminium curve subtracted from the cæsium-aluminium curve gives a difference of 37·4 instead of 36. Similarly, good agreement is obtained in each case except for thallium where the discrepancy is larger. The fact that these curves should agree so well, considering that they represent independent measurements and calculations employing absorption coefficients varying from NH_4 to Tl by a factor of 20, is most striking. The difference between potassium-aluminium and potassium-chromium alum is evident only in the region of 180°, as would be expected. The curves do not at any place drop to zero ordinate values, since as there are so many atoms their fields must overlap. The important question is the interpretation of the peak at about 124°. If this is the $\frac{3S}{4}$ sulphur peak it would represent a displacement of the sulphurs along the diagonal from the centre of the small cube of 34° or 1·98 ångströms toward the trivalent metal atom. If this were the case, the position of the corresponding peak could be predicted using the (110) and (100) plane sets. These curves were drawn giving families similar to those shown in fig. 2. The central peak in these curves, however, indicated a smaller shift of the sulphur from the centre of the small cubes than indicated by the (111) set above. This might well be the case if the peaks were not due to the sulphur alone but rather to the region of maximum density of the sulphur and adjacent oxygen layers.

To test this conclusion various positions might be assigned the sulphur atom and the structure factor computed from the atomic structure factor curves of Hartree *. Since the effect

* Phil. Mag. 1. p. 289 (1925).

of the oxygen falls off rapidly as the diffracting angle increases compared to sulphur, for high orders of reflexion the oxygen may be neglected as an approximation. The mean of these calculations seemed to assign a position to the sulphur shifted about 26/180 or 1·55 ångströms from the small cube centre toward the aluminium. The difference between this value and the peak indicated in fig. 2 is readily accountable by the effect of oxygen atoms if the tetrahedron is properly fixed in its angular position on the cube diagonal, and might be of assistance in deciding between possible arrangements.

This position of the sulphur leads to at least two possible configurations for the remaining atoms, both compatible with dimensional requirements and the crystal symmetry, but perhaps not equally reasonable. In one of these configurations the apex of the SO_4 tetrahedron approaches the aluminium. If the following atomic radii * are assumed: oxygen, 2·7 ångströms; sulphur, 0·6 ångström; aluminium, 1·1 ångströms and monovalent metal, 2·7 ångströms, then the distance between hexagonally close packed layers of oxygen or monovalent metal becomes 2·2 ångströms and there is room for sulphur and also approximately aluminium in the interstices between the oxygen. In the above configuration, however, there would be just sufficient room for the oxygen at the apex of the tetrahedron to touch the aluminium. Toward the monovalent metal there would be just room for three groups of three oxygen atoms: the first, that of the SO_4 group, and the other two the six water molecules ascribed to each cell. Since the SO_4 tetrahedron can take only one angular position to account for the apparent larger shift from the (111) curves, and since space limitations are just satisfied by a hexagonal close packing of the three oxygen groups, the position of every oxygen atom would follow.

There are two objections to this arrangement. The aluminium atom would be left in line between two oxygen atoms; and the water of crystallization would be associated entirely with the monovalent metal, whereas it is perhaps more natural to associate water of crystallization with the smaller atom.

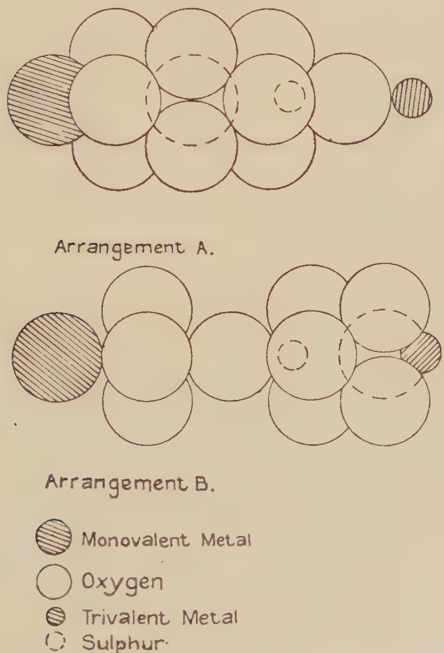
The following alternative arrangement possesses neither of these objections and satisfies the space requirements almost equally well. In this arrangement the SO_4 tetrahedron shifts with its base towards the aluminium. Between the three oxygens of the base of the tetrahedron and the

* W. L. Bragg, Phil. Mag. ii. p. 258 (1926).

aluminium is a closely packed group of three water oxygens, the other three water oxygens lie between the apex of the tetrahedron and the monovalent metal. Six water molecules are thus associated with each metal atom. Since the angular position of the SO_4 tetrahedron on the trigonal axis is limited to one position to give the increased apparent shift for the (111) plane set, so also would be the position of the six oxygens about the trivalent metal. This would not be the case, however, with the six oxygens about the monovalent

Fig. 3.

Possible Arrangement of Atoms along the Trigonal Axis.



metal. It would now be possible to write the general equation for the complete structure factor and assigning different parameters to the oxygens in this last general position to compare calculated and experimental F values for low-order reflexions. However, since the extinction factor plays such an important part in these calculations at small reflecting angles, and since its effect in the alums is uncertain, such calculations are deemed hardly worth while.

The two configurations mentioned above are shown in fig. 3. The positions of the various atoms for the second more probable arrangement (B) are as follows :—

Monovalent metal :					
{0 0 0}	and	three	other	related	positions.
Trivalent metal :					
{·5, 0, 0}	,,	,,	,,	,,	,,
Sulphur :					
{·322, ·322, ·322}	,,	seven	,,	,,	,,
SO_4 oxygen—Vertex :					
{·245, ·245, ·245}	,,	,,	,,	,,	,,
SO_4 oxygen—Base :					
{·304, ·304, ·407}	,,	twenty-three	,,	,,	,,
Water oxygen, trivalent metal :					
{·483, ·483, ·392}	,,	,,	,,	,,	,,
monovalent metal :					
{x, y, z}	,,	,,	,,	,,	,,

R. W. G. Wyckoff has pointed out that in the case of the monovalent metal being NH_4, the only arrangement for the four ammonium hydrogens compatible with the space group is their arrangement in line on the trigonal axis. This was regarded as an arrangement so unlikely as to be considered a case in which the symmetry of the space group was not maintained. In the second configuratien suggested, the necessary room would be found in the close packing interstices on the trigonal axis.

In order to confirm the arrangement suggested here more members of the alum group should be examined, particularly those in which the sulphur is replaced by a heavier element such as selenium.

This opportunity is taken to express appreciation to Mr. W. H. Taylor for taking the rotation photographs, and to Prof. W. L. Bragg for providing facilities for the work as well as kind advice during the investigation.

LXI. *On the Union of Helium with Mercury**. By
J. J. Manley, *M.A.*, *Fellow of Magdalen College, Oxford*†.

1. *Introductory.*

THE wholly unexpected discovery which is the subject of this paper may be conveniently approached by way of a brief review of the experiments which led up to it.

It is well known that when a barometric tube containing its normal column of mercury is moved up and down, electric charges are generated upon the glass. If a little gas be present within the tube a feeble glow is produced, and this is usually accompanied by chemical action and a consequent decrease in pressure. In many cases also the glass walls become stained and ultimately coated with solid matter: this readily happens when the experiment is made with oxygen, nitrogen, or air. But when very pure hydrogen is used, the tube may be oscillated for hours without the production of anything beyond a feeble glow-discharge. If, however, the experiment is greatly prolonged, a narrow annular film having a pearl-like lustre is formed. The substance appears to have but little chemical stability, for on bringing the tube to rest the film gradually vanishes. Chemical analyses showed that in the three cases first cited the solid bodies found within the tube were respectively mercury oxide, a stable nitride of mercury, and a compound containing both mercury and ammonium. The lustrous substance obtained with hydrogen was not analysed: its unexpected transient nature had not been allowed for. But considering the purity of the gas, the chemical cleanness of the tube, and the care taken in purifying the mercury, there can be but little doubt that the substance in question was a hydride of mercury. Possible impurities such as oxygen, nitrogen, or chlorine derived from the glass would each and all form with mercury substances which are at once non-volatile and quite permanent under the ruling conditions.

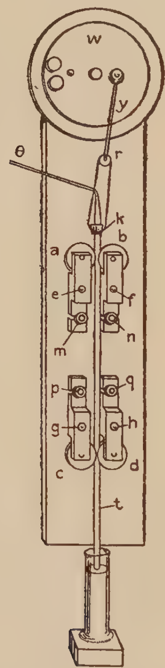
All the experiments just dealt with were made with the apparatus depicted in fig. 1. The barometric tube was set up between rotatable guides and suspended from a large pulley; and this, when driven by a motor, caused the tube to oscillate as required.

* A first paper dealing with mercury helide was communicated to the Royal Society in July 1925. The paper was deposited in the Archives of Burlington House. Also Brit. Assoc. Reports, 1926.

† Communicated by the Author.

This same apparatus was employed for an additional experiment for which pure helium was used. This was done to illustrate the correctness of the views universally held concerning the observed chemical inertness of the gas. Accordingly the tube was actuated for a long time before it was again scrutinized. The result was surprising; for although the lustre of the glass surface was unimpaired,

Fig. 1.



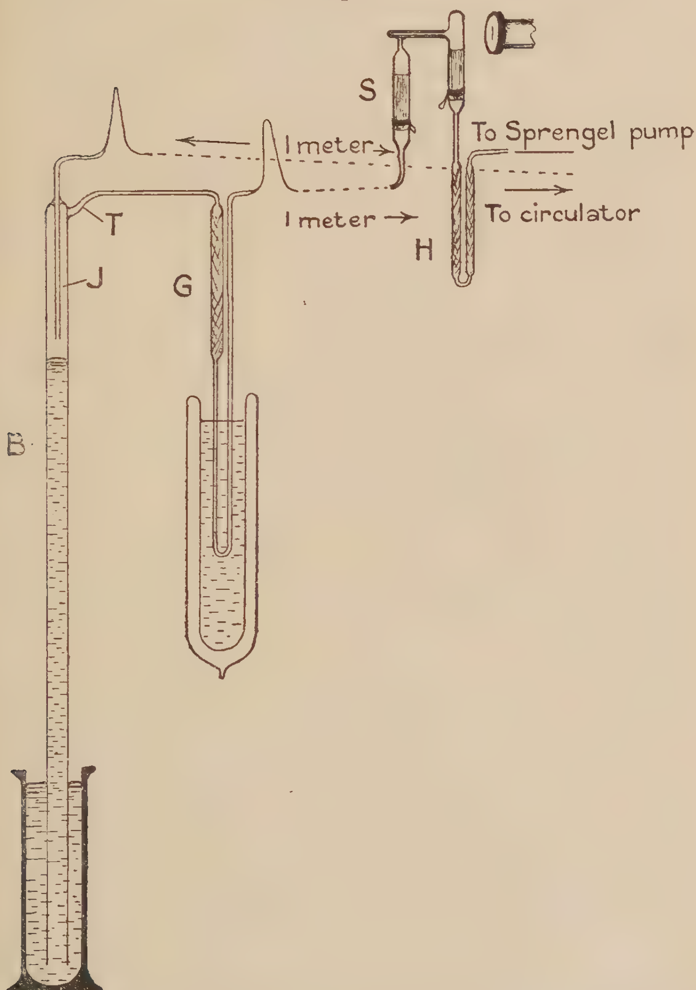
the pressure of the helium had lessened. An *increase* in the pressure could have been explained by assuming (1) that gas had either entered the oscillating tube by making its way along the glass surface from without, or that it had escaped from the mercurial column; and (2) that the remnants of a gas-grown skin had been eroded by the glow-discharge * set up during the experiment. But even these arguments would be untenable, for the intrusion of common gases would result in the formation of solid matter.

In the experiment with helium the initial and final pressures of the gas were respectively 7 and 2·3 mm. The

* Proc. Phys. Soc. xxxvi. p. 288 (1924).

decrease in the original pressure was therefore 67 per cent. It was difficult to account for a change so marked without postulating the formation of a helide of mercury: this view was therefore provisionally accepted, the simple

Fig. 2.



introductory experiments terminated, and plans made for obtaining more complete evidence.

With the simple apparatus of fig. 1 it was obviously impossible to attempt the condensation of the hypothetical helide, and therefore an elaborated form (shown in fig. 2)

was constructed. The new barometric tube was fitted with an injector J and an outlet T; and these, by means of flexible glass capillary tubes 1 m. long, communicated with the corresponding orifices of a circulator * not shown. The chamber G and the U-tube H were filled with gold-leaf: the spectrum tube S was thus guarded against the intrusion of mercury vapour. During each downstroke of the tube B the narrow U-limb attached to G plunged into liquid air. Drying was effected by circulating the helium through a chamber containing purified phosphorus pentoxide. With this apparatus experiments were made as follows.

First, the apparatus was chemically cleaned and dried; then an X-ray vacuum was established, and the gas-grown skins eroded † and removed. Next, pure helium was admitted and circulated for some hours, and then withdrawn. A second portion of pure helium was now introduced and circulated for the purpose of drying. Lastly, the pressure p of the gas when stationary was noted, the circulator restarted, and the motor brought into use. The speed of the latter was such that the barometric tube executed some 7000 or more strokes per hour.

For these experiments p was varied within the limit of 14 and 0·36 mm., and the tube oscillated for many hours; but at no time was any substance discovered within the U-limb of G. It was, however, found that when $p=10$ mm. initially the value slowly decreased to 8 mm.; similarly, when $p=2{\cdot}57$ mm. a gradual decrease to 2·08 mm. was observed.

These results accord with that obtained in the earliest experiment. The synthesis of mercury helide was probably followed by the formation of a gas-grown skin of the compound; and this skin would be densest upon the surface cooled by liquid air. The evidence for this lies in the fact that as the experiment progressed the mercury green line, as seen in the spectrum-tube, increased in strength; also the intensity was considerably enhanced upon the removal of the liquid air. If the observed increase had been due to free mercury, the intensity of the spectral line would have acquired a maximum value at the minimum pressure of 0·36 mm. It was not so; at that pressure the line was very faint.

From the experiments just detailed three facts emerge.

* Proc. Phys. Soc. xxxviii. p. 129.
† Proc. Phys. Soc. xxxvi. p. 288.

They are :—

(1) At low pressures and in the presence of a glow-discharge, helium is capable of uniting with mercury.

(2) The synthesized helide is not condensed, but remains gaseous, even at the temperature of liquid air.

(3) The helide, in common with other gases, gives rise to gas-grown skins.

It may here be remarked that the formation of a gas-grown skin partially accounts for the decrease in pressure noted during the synthesis.

An attempt was now made to devise more efficient synthesizers. Some of those are described in the next section.

2. *Various Synthesizers.*

As the helide appeared to be formed in a glow-discharge, synthesizers within which the glow could be produced and varied in intensity were made and tested.

The first of the new synthesizers was a narrow barometric tube surmounted by another 57 cm. long and 22 mm. wide. To the wide portion two external electrodes of tinfoil were attached, the one at the upper end and the other at the lower. The wide limb was also given two side-tubes; these communicated with an apparatus for circulating the contained helium. The spectrum tube S of fig. 2, used for detecting mercury, was, together with its guard-tubes, included in the circuit. With this apparatus many experiments were made, but in no instance was the pressure of the helium changed; also the mercury green line was invariably faint or altogether invisible. The instrument was thus found to be ineffective.

A second synthesizer in which the glow-discharge was produced between parallel electrodes of aluminium, and also a third having mercury electrodes, were equally ineffective; but a fourth, which may now be described, yielded an important result.

The synthesizer which contained 25 c.c. of mercury was a glass tube 35 cm. long and 18 mm. wide placed horizontally in a movable cradle. Its two ends were drawn out to form short narrow limbs, which were bent upward and fused to vertical glass capillary tubes: these last were about 1 m. long, and their upper portions were shaped like a horizontal V. Formed thus, the tubes were not liable to fracture. The capillary tubes communicated, the one with the inlet

and the other with the outlet of the gas circulator. The apparatus was rendered complete by the inclusion of a Sprengel pump, a charcoal chamber which could be immersed in liquid air, and the two gas chambers of a Jamin interferometer. The several sections of the apparatus were in this, as in all other cases, joined by fusion: this is highly important. With the aid of mercury traps it was possible to arrange for the circulating helium to flow serially through the two interferometer chambers, or the contents of one chamber could be isolated and used as a standard of reference for the helium circulating in the other.

To begin with, the apparatus was highly exhausted and then washed out with helium generated from thorianite. The gas on its way in passed through charcoal cooled by liquid air, and was thus purified. The apparatus was again exhausted, then suitably charged with helium, and the gas continuously circulated for a considerable time. In this way traces of air were absorbed and retained by the charcoal cooled by liquid air. The purity of the helium was tested as follows.

First, the circulator was stopped, the reference chamber of the interferometer closed, and the position of a selected fringe adjusted and noted. Next, the circulator was again used, then brought to rest, and the position of the fringe re-observed: as the fringe had not shifted, the gas was homogeneous and ready for use. At this stage the pressure of the helium was measured, the gas re-circulated, and the cradle containing the synthesizer rapidly moved to and fro. By trial it was found that when the cradle executed some 2000 strokes per hour the mercury within the synthesizer remained almost stationary: the motor was therefore adjusted for that speed. It will be observed that in this experiment the required glow-discharge was, as in that with the barometric tube, produced by friction. Proceeding thus, experiments were made with helium at pressures ranging in value from 4·6 to 0·4 mm. Variations in the density of the gas were indicated by the interferometer only when $p=1{\cdot}3$ mm. With helium at that pressure, the sighted fringe first shifted negatively by one-half of its width and then for a time remained stationary; but as the experiment progressed, the zero position was regained and then finally entirely over-passed. Taking the width of a fringe as measured by rotating the compensator as $60'$, the observed respective displacements were $-30'$ and $+66'$. The first movement of $-30'$ indicated a *decrease* in the density

of the gas, and the second or $+66'$ an *increase.* Bearing in mind the fact that the interferometer was connected with the synthesizer by some 3·5 m. of tubing, much of which was of capillary dimensions, the observations are readily and probably correctly interpreted as follows

On starting the experiment, helium begins to combine with mercury vapour ; the synthesis proceeds (probably at a diminishing rate) until some small and limiting percentage of helium has been formed. If the experiment is prolonged the total helide is not thereby increased, for here, as in the case of the formation of ozone, a balanced action ultimately obtains. Initially, the known diminution in the pressure of the gas is local, the locality being that of the active synthesizer. In due time, however, the decrease in pressure is manifested throughout, and consequently the density of the helium in the testing chamber of the interferometer is lessened ; in response to this change the sighted fringe shifts as stated. Next, as a result of the continued circulation of the gas, the mixture of helium and helide enters the interferometer ; the original density of its contents is thus first gradually restored and finally surpassed. Hence the observed second or positive shift of the fringes.

The conclusion here reached was confirmed by another experiment, similar in form, but carried out with a stationary synthesizer armed with external electrodes. In this experiment a spectrometer was used in conjunction with the interferometer. The evidence of the one agreed with that of the other.

Other forms of apparatus were tried, but all, with the exception of that to be described immediately, proved useless. In the next section is given an account of the method adopted for a first quantitative analysis of mercury helide.

3. *The Apparatus.*

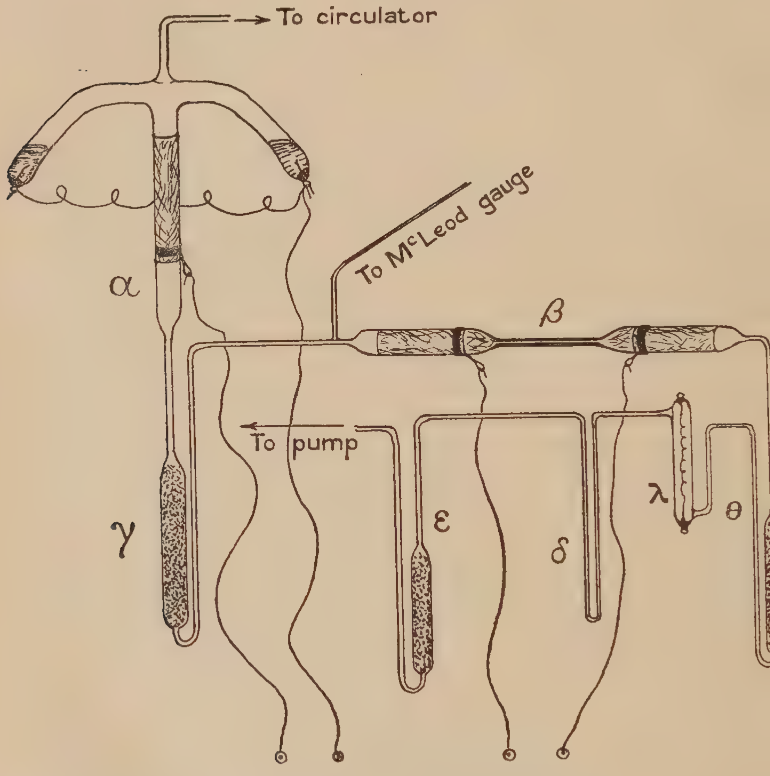
The earliest attempt to determine the chemical composition of the helide was made with the aid of the apparatus shown in fig. 3, wherein α is one synthesizer having both mercury and tinfoil electrodes, and β another fitted only with external electrodes of tinfoil. In this latter the wide portions covered by the electrodes contained platinized asbestos loosely arranged and previously purified. δ is a U-tube of small bore, and γ, ϵ, and θ chambers filled with charcoal. The heater λ was a tube 10 cm. long and 15 mm.

wide, having a spiral of platinum wire. The wire was 0·1 mm. in diameter, and its ends were welded to platinum terminals. The apparatus was prepared for use as follows.

4. *Preliminary Treatment.*

First, a high vacuum was established and maintained for 6 days. During that time the gas-grown skins upon the

Fig. 3.



interior were electrically eroded and removed; the charcoal chambers were also strongly heated. Next, pure helium was introduced and left undisturbed for 10 days; it was then pumped out, and the new gas-grown skins erupted and ejected. A further charge of helium having been admitted, the circulator was kept in action for a time and the gas examined; the spectrum was quite free from air-lines. Lastly, this helium was also pumped off and a final charge

introduced. The charcoal chambers ϵ and θ were now immersed in liquid air, the helium circulated, and a flame passed to and fro over the limbs extending from ϵ to θ; also the platinum spiral was raised to a bright red heat. The portion $\epsilon \rightarrow \theta$ was thus rapidly freed from mercury, the absence of which was ascertained spectroscopically. When the helium had acquired a constant pressure (12·1 mm.) the preparations were complete. The synthesis and analysis of the helide were then carried out as described below.

5. *Synthesis of the Helide.*

A maximum quantity of helide was formed by activating the synthesizers with a coil yielding a 1-inch spark. The synthesizers were sometimes used singly and at other times conjointly. When α alone was used, the pressure of the circulating helium remained unaffected; but on bringing β into action alone or in conjunction with α, the pressure declined and finally attained a minimum and constant value. The constancy of the new pressure was taken as indicating the impossibility of carrying the synthesis further. The coil was therefore silenced as a preliminary to the next step.

6. *Decomposition of the Helide.*

Tentative experiments not described here had shown that, on passing the mixture of helium and helide through the active heater λ, the minimum pressure resulting from the action of β gradually gave place to one of larger value, but the new final pressure, although approximating to the original, seldom equalled it. The same experiments also showed that the increasing pressure was invariably accompanied by an accumulation of mercury in the U-tube δ. The method of analysis was therefore as follows

First, the U-tube δ was immersed in liquid air and the pressure of the gas determined; then the spiral λ was raised to and maintained at a bright red heat, the circulator started, and from time to time the pressure p re-determined. When there was no further change in p, a flame was passed over the body of λ and its limbs until the whole of the mercury liberated from the helide had been driven into the lower portion of δ; the limbs of δ were then closed by softening the glass, and the U-tube with its contents drawn away from the main apparatus and finally prepared for weighing.

7. *Determination of the Weight of the Mercury.*

After δ had been withdrawn the bend was placed in liquid air, the limbs heated, and finally sealed at points some 3 inches above the bend and the superfluous tubing removed. In this way the minute quantity of mercury was collected within a container of small volume. Next, a counterpoise K similar in all respects to δ was made, and its volume repeatedly altered until it differed from that of δ by the negligible quantity of ·011 c.c.

We may here observe that in determining the mass, which was less than 0·3 mg. of mercury, exceptional difficulties arise; and it will be seen that very inaccurate conclusions may be reached if the containing tube is first weighed, then notched with a cutter and fractured for the removal of its contents prior to a final weighing. The correctness of this view is borne out by the results of an actual experiment, in which notching and fracturing caused the respective losses of ·0043 and ·015 mg. Such errors were in the present case avoided by opening δ in dry carbon dioxide-free air before commencing the weighings. After the first weighing the mercury was removed by dissolving it in nitric acid, the tube washed out with "conductivity" water, and then dried and re-weighed.

In carrying out the several weighings, all the precautions which I have shown to be necessary and advocated elsewhere were taken: it will therefore suffice if brief mention be made of the following salient points:—

(*a*) Use was made of a balance having a beam cantilever in type and protected *. For a given temperature the instrument had a constant sensitivity for all loads. The sensitivity, and also the temperature-coefficient of the balance for the load to be imparted, were each determined shortly before the mercury obtained from the helide was weighed. The movements of the balance were observed and measured optically, and for that purpose the apparatus included a plane mirror fixed to the centre of the beam, and a telescope for viewing the pointer of light, which was 6 m. long.

(*b*) After the tube δ and its counterpoise K had been wiped and suspended from the stirrups, and before their relative weights were determined, both were washed *in situ* by streams of dry and carbon dioxide-free air.

(*c*) For measuring the several weights, the method of Gauss was used. The weight of δ + mercury and of δ alone

* Thorpe's 'Dictionary of Chemistry,' new edit. Article "Balance."

were the means of several series of weighing duly corrected.

Proceeding as outlined above, it was found that the weight of the combined

$$\underline{\text{Mercury} = 0{\cdot}236_1 \text{ mg.}}$$

8. *Determination of the Combined Helium.*

For the synthesis of mercury helide, pressures ranging from 12·1 to 0·6 mm. were tried. Positive results, as indicated by a decrease in the pressure p, were obtained only when p was approximately 6, 1·9, or 0·6 mm. Accordingly syntheses followed by analyses were effected at each of these pressures, the results summed, and the totals treated as for one complete experiment. The data obtained are given in the following table.

TABLE I.

Exp.	Pressure of Helium. (a) Initially.	(b) After synthesizing.	(c) After analysing.	Diffs. (c)−(b).	Weight of helium in helide.	Total weight of helium in apparatus.
1.	6·24 mm.	5·75 mm.	6·02 mm.	0·27 mm.	$\cdot017_8$ mg.	0·378 mg.
2.	6·11 „	5·91 „	6·11 „	·20 „	$\cdot012_8$ „	„ „
3.	1·96 „	1·85 „	2·05 „	·20 „	$\cdot012_7$ „	·121 „
4.	·595 „	·561 „	·595 „	·034 „	$\cdot002_3$ „	·036 „
5.	·595 „	·561 „	·581 „	·020 „	$\cdot001_4$ „	„ „

Hence total weight of combined

$$\underline{\text{Helium} = \cdot047_0 \text{ mg.}}$$

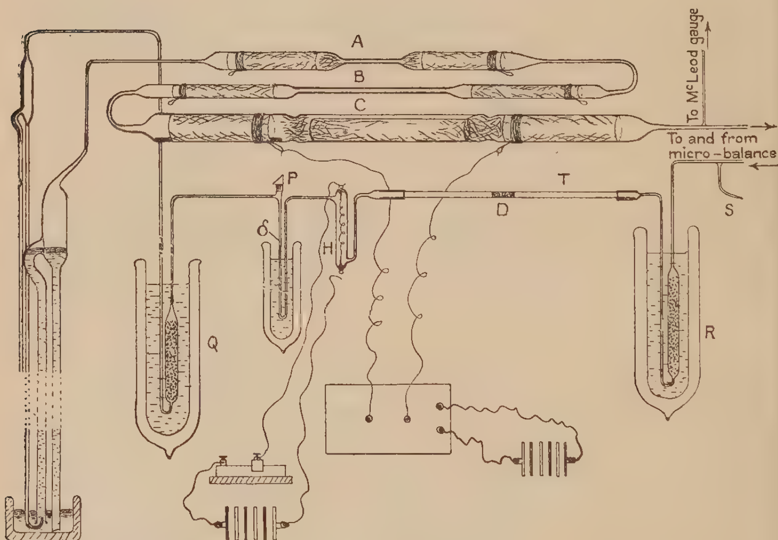
From the above we find that 200·6 parts by weight of mercury combined with 39·94 parts by weight of helium. It therefore appears that the simplest formula for the helide is

$$\underline{HgHe_{10}.}$$

In calculating this formula, the view held was that on activating the synthesizers the *formation* of a gaseous helide did not in itself cause any change in volume, and that the diminution in p was consequent upon the growth of a somewhat volatile skin of helide upon the internal surfaces of the apparatus in general. Hence in the presence of a fully-developed skin it was impossible to do more than synthesize an additional but infinitesimal quantity of helide, the pressure of which balanced the tension of the skin. When the gas was circulated and the heater used, the

minute quantity of free helide was decomposed and the tension of the skin left unbalanced. Under these conditions the skin continuously reverted to the gaseous state and was decomposed; and as the decomposition progressed, the original pressure was either partially or wholly restored. Such partial restorations were observed in exps. 1 and 5, and whole ones in exps. 2 and 4. In exp. 3 the final pressure overpassed the initial. This was probably due to the decomposition of some helide remaining at the conclusion of exp. 1.

Fig. 4.



Assumptions other than those just stated appear to lead to formulæ for the helide even less acceptible than that based upon my hypothesis.

We may now describe the apparatus and methods used for another and similar determination.

9. *Second Quantitative Analysis.*

Before proceeding with the second quantitative analysis of mercury helide, important changes were made in the apparatus, and the synthesizers formerly used replaced by three others, A, B, and C; these were constructed and disposed as shown in fig. 4. In the new apparatus the helium in circulating passed in the direction A⟶B⟶C.

The synthesizer A was similar in form to, but larger than, β of fig. 3. Its wide limbs were, like those of β, filled with loose platinized asbestos. The second synthesizer, B, differed from A in that it contained no asbestos ; also its capillary tube was twice as long and of larger bore. C was a tube 34 mm. wide and 58 cm. long, and within it were placed loose wads of platinized asbestos and a little pure mercury. All the synthesizers were fitted with external electrodes. A new heater, H, displaced λ of fig. 3 ; also the sensitivity of the spectroscopic test for mercury was greatly increased by the use of a right-angled prism P mounted as shown *. This device gave the spectrometer an end-on view of the vertical tube when the glow-discharge was set up for the test. The apparatus was rendered complete by the inclusion of an Aston micro-balance (not shown in fig. 4) and a silica tube T having a tightly-fitting plug, D, composed of fine and purified asbestos fibre. In this, as in the earlier experiment, all gas-pressures not exceeding 7 mm. were measured with a McLeod gauge having an accuracy of ·0001 mm. Larger pressures were determined with a cathetometer. The Sprengel pump and the circulator which formed part of the apparatus were those described in former papers †. The second experiment was commenced only after the complete apparatus had been prepared with all the care observed for the first. The several charges of helium were obtained from powdered thorianite, which was heated in an attached silica tube. On its way in, the gas passed through charcoal cooled by liquid air, and when the final charge of helium had been introduced, the silica tube and its charcoal chamber was sealed off at S. The apparatus was then ready, and the experiment was carried out as follows.

First, the charcoal chambers Q and R were surrounded by liquid air, the circulator started, and the heater and its limbs, including δ, freed from mercury. When the pressure p was constant, the micro-balance was read and the synthesizers activated for 4 hours. During the synthesis, p was but slightly affected. Next, the action of the synthesizers was arrested, the micro-balance re-read, δ immersed in liquid air, and the heater used for 11 hours. Again p varied but little. When the helide had been decomposed, the chamber of the micro-balance and its attachments were by means of mercury traps shut off from the main apparatus, and the compressor operated until the density of the helium as indicated by the micro-balance equalled that previously shown for the mixture

* Proc. Phys. Soc. xxxviii. p. 127.

† Proc. Phys. Soc. xxxvii. p. 142.

of helium and helide; the pressure corresponding to this density was then measured. Finally, the mercury liberated from the helide was collected in the bend of δ, then sealed up and its weight determined. The weighings were carried out with additional refinements lately introduced*. With the aid of those extra refinements the weight of the mercury was, it is believed, determinable with an accuracy of $\pm \cdot 0005$ mg. The following table contains the summarized data.

TABLE II.

Mean pressure of the gas before the synthesis	= 5·46 mm.
" " " during " "	= 5·44 "
" " " after the analysis	= 5·46 "
Final mean	= $5{\cdot}45_3$ mm.
Weight of mercury derived from the helide	= $0{\cdot}271_4$ mg.
" helium present in the apparatus	= $1{\cdot}771_6$ "
Total weight of helium and helide	= 2·043 mg.
Calculated density of mixture in terms of helium $= \frac{2043}{1771_6}$	= 1·153
Density as measured by the micro-balance	= 1·148

The above observations and data receive a ready explanation on the assumption that in the second quantitative experiment another helide having the empirical formula

$$HgHe$$

was synthesized. The line of argument here adopted is, as will be seen, similar to that used in the case of mercurous chloride, HgCl.

It may however be said that another formula, namely $HgHe_2$, is also in harmony with the data of Table II. The mono- and di-helides of mercury differ in their molecular weights by 2 per cent. only, and the total helide present for quantitative analysis was never greater than 3/100 c.c. It will therefore be seen that the effect of substituting $HgHe_2$ for HgHe is, in so far as the density of the mixture is concerned, inappreciable or nearly so. Hence we may accept the formula $HgHe_2$ as being more in accord with probability. For this view I am indebted to Dr. Sidgwick.

We have already noted that during the synthesis and analysis the respective mean variation of − and +0·2 mm. occurred in p. These changes seem to show that a little of

* Proc. Phys. Soc. xxxix. p. 444.

the other helide $HgHe_{10}$ was first formed and subsequently decomposed; but in the absence of definite proof, this point is not further pressed. All attempts made with the new apparatus to prepare $HgHe_{10}$ in quantities larger than that here suggested ended in failure.

10. *On the Absence of Floating Particles.*

In the first quantitative experiment the decrease in the pressure of the helium, together with the failure of the helide to condense, readily leads to the supposition that the compound might be diffused as floating solid matter; but in that case it should be possible to remove at least some of the particles by filtration. It was for testing this view that the silica tube with its asbestos plug was inserted between R and H, as shown in fig. 4. The plug was at the outset strongly heated *in vacuo* and also stripped of gas-grown skins. It was in use throughout the second quantitative experiment just described. Had particles been arrested by the filter-plug, additional helide would presumably have been synthesized, and consequently the pressure of the helium would have diminished continuously. Also, on heating the plug, the arrested helide would have been decomposed and additional mercury obtained. Experimentally, the reverse of this was observed; the pressure was, as already stated, practically unaffected, and when the plug was heated to redness no mercury was detected. Hence we again came to the conclusion that mercury helide is a gaseous and not a solid compound. Two other points yet remain and call for investigation—namely, the question of the possible introduction of mercury (*a*) from the platinum spiral, and (*b*) from the charcoal chambers immersed in liquid air.

11. *On the Absence of Mercurial Impurities.*

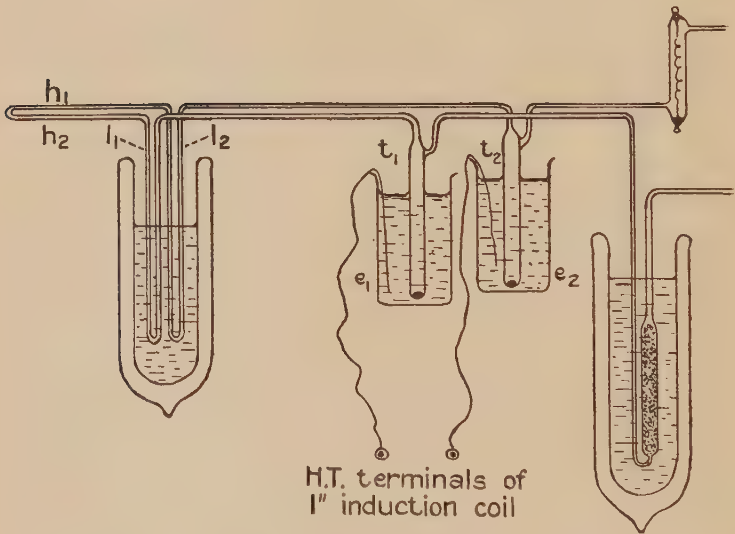
The difficulties of admitting the probability of the union of helium with another element are for the moment so great that we are tempted to accept any explanation other than the true one to account for the appearance of mercury in the U-tube δ. Of the possible explanations, two only call for immediate consideration. It may be urged (1) that the mercury was derived from the platinum spiral of the heater, and (2) that when the synthesizers were active, electric discharges occurred in the charcoal chambers and eroded the solidified mercury, and that resultant particles were then to some extent carried forward into δ by the circulating

helium. With regard to (1), an inferential reply is contained in the preceding sections. It will therefore suffice to note that an essential part of the preparation of the apparatus consisted in circulating the helium and heating the chamber containing the white-hot spiral for some time after mercury could no longer be spectroscopically detected. It will thus be seen that explanation (1) is valueless.

For testing the validity of (2), experiments were made as follows:—

The main apparatus of fig. 4 was opened at a convenient point and the auxiliary apparatus of fig. 5 inserted. The tubes t_1, t_2 with their mercury contents were given external

Fig. 5.



electrodes e_1, e_2 of water, as shown. The completed apparatus was first prepared as usual, and then charged with helium at a pressure of approximately 5 mm. Next, the two U-tubes l_1, l_2 were immersed in liquid air, the helium circulated continuously, and the horizontal limbs h_1, h_2 heated until they were free from mercury. A *bright* glow-discharge was now set up and maintained within the auxiliary apparatus for 1 hour. On re-examining the limbs h_1, h_2, nothing beyond an occasional glimpse of the mercury line, dim and uncertain, was obtained. A second and similar experiment made after mercury had been distilled

into the U-tubes l_1, l_2, and boiling water substituted for cold in the electrode vessels led to an equally negative result. It was thus decisively shown that any mercury entering the liquid air-cooled tubes is completely arrested and retained, even in the absence of impeding charcoal. The tentative explanation (2) is therefore like (1) untenable. But apart from these proofs, it would have been most remarkable had mercury transported at random possessed in two successive instances just those masses required for such precise agreement with related data. Such coincidences are, of course, altogether highly improbable. Some concluding experiments carried out as the result of a suggestion made by Professor Henri, of Zurich, must now be described.

12. *Experiments with a Quartz Spectrograph.*

During a discussion of the problem, Professor Henri expressed the opinion that mercury helide would give rise to an absorption line in the ultra-violet region, and, further, that the wave-length of the said line would be something like 2500. As such additional evidence was highly desirable, the apparatus of fig. 4 was altered and the twin 1m chambers* of a quartz spectro-photometer substituted for the silica tube T; also the micro-balance was cut out, and the gap thus left closed by a short tube.

For producing the required ultra-violet light, use was made of a 10 in. coil supplied with a current (fed through a motor-driven mercury interrupter) of 9–10 amps. The discharge points were of pure cadmium and the gap was 3 mm. The spark was intensified by a large Leyden jar, and the rays of light rendered parallel with a 2 in. quartz lens. After the light had traversed the spectro-photometer, the two emergent beams entered the slit of a quartz spectrograph and were photographically recorded. The procedure was as follows.

First, the whole apparatus was prepared as for other experiments and then charged with pure helium. Next, the helium was circulated for 2 days and a series of photographs taken. In all these photographs the mercury absorption line 2537 was, as seen in each pair of spectra, equally faint, and in the last instance the line was no weaker than in the first. (This persistence of the line is considered presently.) As the absorption line, though faint, remained unchanged, the inlet and outlet tubes of the lower or reference chamber S

* The gas flowed through the chambers as two parallel and not as two serial streams.

were softened by a flame and so closed. The contents of S thus served as a standard.

With the helium still circulating, the synthesizers were now activating for some hours during each of 5 successive days; also photographs of the twin spectra were periodically taken. It was thus found that the intensity of the mercury absorption line of the sealed reference chamber increased, and ultimately assumed a constant value. In the testing chamber the same line, invariably weak, was in some cases more in evidence than in others. In these experiments the pressure of the helium was varied within the limits of 11·5 and 6·38 mm.

A scrutiny of all the plates for the expected new absorption line showed that in 3 cases only was any such line present. In one of these a line of WL 2276 was found; but as it was common to both spectra, it was judged to be due to extraneous matter. In the other two cases the line was one and the same; it was very weak and not sharply defined, and its WL was 2624 *. The line appeared first when the pressure of the helium was 11·5 mm., and again when $p=6{\cdot}38$ mm. In each instance the weak mercury absorption line was, as usual, also present. An attempt was now made to obtain a more marked effect; and for that purpose the apparatus was reconstructed so that by means of added mercury traps the testing chamber T could be closed, and then with the aid of an attached Sprengel pump the gaseous contents of the main apparatus M transferred to T and there be retained for spectrographic analysis. From the known volumes of M and T the sensitivity of the test was thus theoretically increased fourfold.

With this apparatus syntheses were effected in the usual way, and the product together with the free helium concentrated and then examined with the spectrograph. All the results were purely negative, and in no case was there any trace of the new absorption line. Whence it appears that if the line 2624 was really due to mercury helide, the conditions under which the compound can exist when traversed by ultra-violet light were obtained by chance, and are at present unknown.

13. *On the Persistence of the Mercury Line* 2537.

Attention has already been drawn to the fact that the mercury absorption line of WL 2537 is invariably present

* This line has been re-measured by Messrs. A. Hilger, who find its WL to be 2638.

in spectra obtained with the test chamber. As the inlet and outlet tubes of the chamber were guarded by U-tubes placed in liquid air, it was not easy to discover from whence the mercury came. For investigating this, the apparatus was again altered and a spectrum tube having external electrodes inserted between the exit of the chamber T and its guard-tube. These changes having been effected, the presence or absence of mercury within the guarded portion of the apparatus could be ascertained (*a*) by the absorption line 2537 and (*b*) by the highly characteristic emission line 5461. The following experiments were then made :—

(1) First, the apparatus was highly exhausted, the guard-tubes Q and R (fig. 4) immersed in liquid air, and the whole left at rest. Two days later, the vacuum being high, it was impossible to activate the spectrum tube. A photograph of the twin spectra for the chambers S and T was now taken; this proved that mercury vapour was quite absent from the testing chamber T.

(2) Next, a second photograph was taken whilst the chamber T was strongly heated. In this case also mercury was entirely absent. These results attest the perfect efficiency of the guard-tubes, and at the same time show that whether mercury be present as vapour or in the form of a skin, it is completely withdrawn and prevented from re-entering the chamber and its attached spectrum tube.

(3) Having now freed the testing chamber from mercury, the pure helium was returned to the apparatus and circulated; also photographs of the twin spectra were again periodically taken. All the spectra due to the light passing through T again contained the mercury absorption line 2537. The line, although weak, was invariable. At this stage the heater was used for disintegrating any helide that might be present. The luminosity of the mercury line was not thereby affected.

(4) In the next experiment the circulator, synthesizers, and heater were used for 75 minutes. During this period additional photographs were taken and the spectrum tube frequently viewed with a spectrometer. It was found that the absorption line was but slightly strengthened, whilst the green emission line rapidly increased and finally became very bright *.

The results of the experiments just described led me to conclude that mercury helide in minute quantities is

* To avoid possible misunderstanding, I would remark parenthetically that the oft-mentioned absorption line 2537 was in no case other than what one would designate as "rather weak," "weak," or "very weak."

formed so readily that it is well-nigh impossible to manipulate dry and pure helium over mercury without producing some infinitesimal trace of the compound. The proof for this lies to a large extent in the evidence of the above-cited experiments (3) and (4). That evidence we now briefly review.

14. *Review of Results of Experiments* (3) *and* (4).

When experiment (3) was started, the chamber T and its spectrum tube were, as I have shown, free from mercury. Soon after commencing the circulation of the helium (the synthesizers being idle), the chosen mercury absorption and emission lines were readily detected, the one by the spectrograph and the other by the spectrometer. That the detected mercury could not have passed through the guard-tubes has been conclusively shown by the experiments of section 11. Hence the most acceptable explanation is found in the assumption that mercury helide is synthesized not only in the fall-tube of the Sprengel pump, but also during the ascent of the bubbles of helium in the barometric column of the circulator *. But if this be the whole truth, we should, according to Prof. Henri, expect to find an absorption band or line appropriate to the helide recorded by the spectrograph; instead of which we obtained, in every case but two, the absorption line characteristic of mercury. Apparently the only possible explanation is that the helide, on traversing the ultra-violet light in the testing chamber, is thereby so quickly resolved into its component elements that in general it fails to leave any legible record of its existence. This explanation receives support from the fact that on using the heater towards the conclusion of experiment (3) the mercury line was not intensified. Had the heater been more effective than the ultra-violet light, the absorption line must have been strengthened. This, as we have already stated, was not the case.

We next note that the evidence of experiment (4) is in complete accord with that of experiment (3). The use of the synthesizers would naturally result in the production of a maximum quantity of helide and a consequent though not necessarily marked intensification of the mercury absorption line. That this line could in no case be other than "weak" is clear from the following.

The volume of the gaseous contents of the apparatus was

* The necessary glow-discharges are, as is well known, produced as the mercury drops in the fall-tube, and again when the liquid in the barometric column of the circulator is disturbed.

at this time approximately 1L. and that of the testing chamber 38 c.c. Taking the weight of the combined mercury as 0·27 mg., and assuming this to be uniformly distributed, the mercury in the testing chamber was not more than $0{\cdot}27 \times 38/1000$ or 1/100 mg. Of the light coming through the testing chamber, a small fraction only entered the spectrograph to be photographically recorded; and this being so, the invariable weakness of the absorption line is at once understood. In section 12 we observed that the very weak mercury absorption line 2537 of the standard chamber slowly developed and finally became fairly strong and constant. In accordance with the views already expressed, the strengthening of the line was due to a natural and slow decomposition of the helide, accelerated and completed by the passage of ultra-violet light. Brief allusion may now be made to some experiments with argon.

15. *Experiments with Argon.*

With the object of still further testing these conclusions, a series of experiments similar in all respects to those made with helium were performed with argon*. Certain impurities suspected of being present were removed by sparking the gas between "heavy" poles, the one of aluminium and the other of magnesium, as recommended by Merton and Pilley. For an attempted synthesis, the pressure of the argon was varied within the limits of 14 and 2 mm. The pressure of the argon was unchanged, and in no case was mercury discovered in the receiving U-tube of the heater. From this it is quite clear (1) that argon did not combine with mercury, and (2) [and this for the moment is more important] that mercury was neither mechanically or electrically transported into δ. This last affords additional proof that the mercury found in δ during the experiments with helium resulted, as we have already seen, only from the decomposition of the gaseous helides $HgHe_{10}$ and HgHe.

Further confirmation of the correctness of my results may be found in the evidence of those interesting experiments carried out by Boomer in the Cavendish Laboratory. Boomer has shown † that, under the particular conditions he describes, the helides of some five elements, including

* For the argon used in these experiments, I am indebted to Mr. Bolton-King.

† Proc. Roy. Soc. A, cix. p. 198 (1925).

mercury, are probably formed. They appear as solids, and are unstable except at low temperatures.

In conclusion, I desire to thank Prof. Lindemann, Dr. Sidgwick, and Dr. Freeth for their interest and assistance. I have also to acknowledge my indebtedness to Prof. Soddy, through whom Messrs. Brunner Mond & Co. made a generous grant. That grant enabled me to purchase the quartz spectrograph and also a 10 in. coil for testing the prediction made by Prof. V. Henri.

Daubeny Laboratory,
Magdalen College, Oxford.

LXII. *The Tangent Lens Gauge Generalised* *.

By Alice Everett, *M.A.* †

THIRTY years ago the Philosophical Magazine (vol. xliii. p. 256, 1897) published a description by the late Prof. G. J. Burch, F.R.S., of a simple home-made tool for measuring the curvature of a convex lens, which he named the "Tangent Lens Gauge." It was intended to furnish laboratory exercise for students.

Essentially, it consists of a pair of plate-glass slips joined so as to form a shallow inverted trough which is laid upon the surface under test. The two points of contact, where the plane surfaces touch the sphere, can be seen by reflected light as centres of Newton's ring systems, and the length of the chord joining these points can be measured by the aid of a measuring microscope fitted with a "vertical," or down-tube illuminator. The required radius of curvature is then found by multiplying the chord by a constant factor, and applying a correction, also constant, for refraction. The device is not applicable to concave surfaces.

Recently, in ignorance of Prof. Burch's paper, I chanced to hit upon the same idea, and would here point out that it can be adapted to measure either concave or convex surfaces by employing a tool with spherical, instead of plane, glass faces. A simple arrangement which meets the case is a pair of similar plano-convex lenses fixed edge to edge with their flat faces in one plane. As means of attachment, two parallel, narrow glass strips cemented to the flat faces will serve. These strips should be as far apart as possible, so as

* A previous note appeared in 'The Optician,' Jan. 30, 1925, under a pen-name.

† Communicated by the Author.

to leave the central portions of the lenses free. If this twin combination is placed with its two curved surfaces in contact with the surface under test (it may be secured by plasticene pellets), then the two points of contact, and their distance, d say, apart, can be found as in Burch's method. But the correction for refraction will not be constant in this case.

From the fact that when two spheres touch the point of contact lies on the line of centres, it easily follows that

$$\frac{1}{r}+\frac{1}{R}=\frac{k}{d},$$

where r is the required radius of curvature of the surface under test, R the radius of curvature of either of the twin lenses, and k a constant which can be found by applying the tool to a plane surface. With the usual convention that r is to be taken negatively for concave curvature, the formula is applicable to either a convex or concave surface.

A rough and ready demonstration can be made on spectacle lenses from a test-case, with the naked eye and a pocket scale. The central dark spot of Newton's ring system can easily be seen at the points of contact on applying gentle pressure, though the coloured rings may be invisible. The spot is readily distinguished from dust specks by its sharply circular form.

Riverside,
Sunbury-on-Thames.

LXIII. *A Note on the Dispersion of Methane.*

By T. H. HAVELOCK, *F.R.S.**

1. IT has been commonly assumed, in various connexions, that the hydrides FH, OH_2, NH_3, CH_4 may be regarded as neon-like ions F^-, O^{2-}, N^{3-}, C^{4-} deformed or perturbed by one or more hydrogen nuclei. For example, Fajans and Joos † give the following comparison of molecular refractivities :—

Ne.	FH.	OH_2.	NH_3.	CH_4.
1·0	(1·9)	3·76	5·61	6·55

with estimated values for the hypothetical free ions :

F^-.	O^{2-}.	N^{3-}.	C^{4-}.
2·5	7	(22)	(80)

* Communicated by the Author.

† K. Fajans and G. Joos, *Zeit. für Phys.* xxiii. p. 1 (1924).

The inference is that CH_4 is a member of this series of hydrides with a structure similar to the other members.

Instead of considering only refractivity, let us take into account also the optical dispersion. We shall use the simplest form of dispersion formula :

$$n^2-1=C_0/(p_0{}^2-p^2). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For simple gases under consideration this is sufficient for our purpose, and we take the constants C_0 and p_0 to express approximately the refractivity and dispersion. Cuthbertson has given his experimental results for gases in this form, and we collect his values of the constants in the following table :—

Gas.	$C_0\times10^{-27}$.	$p_0{}^2\times10^{-27}$.
Ne	5·1865	38916
FH	—	—
OH_2	5·2540	10697
NH_3	5·9316	8135
CH_4	10·0554	11689·3

. . . (2)

As regards Ne, OH_2, and NH_3, we note the approximately constant value of C_0 and the regular decrease in p_0, both of which points confirm and bring out more clearly the similarity of structure from the optical point of view. No doubt FH would also fit into this scheme ; we have no knowledge of its dispersion or refractivity in the gaseous state, but if we assume the estimate 1·9 for its molecular refractivity given by Fajans and Joos, and also assume the value of C_0 to be $5{\cdot}2\times10^{27}$, then the corresponding value of $p_0{}^2$ is 20703×10^{27}.

On the other hand, for CH_4 we see that the inference from refractivity alone was illusory; C_0 is nearly doubled and p_0 is also increased, and CH_4 clearly does not fall in with the sequence in (2).

In making this comparison in a recent paper *, I remarked that earlier experiments on the dispersion of methane by S. Loria could be expressed by a dispersion formula (1) with $C_0=6{\cdot}314\times10^{27}$ and $p_0{}^2=7373{\cdot}8\times10^{27}$; and therefore further experimental evidence seemed desirable. Since then, further work has been published which confirms Cuthbertson's formula in its general character. Friberg †

* Phil. Mag. iii. p. 444 (1927).

† S. Friberg, *Zeit. für Phys.* xli. p. 378 (1927).

has studied the dispersion of ammonia and methane over a large range of wave-length extending from 5462 Å. to 2302 Å. It is true that a simple two-constant formula is not sufficiently accurate for this wide range; but that need not concern us here. Friberg gives for methane a two-constant formula which covers this range surprisingly well, namely

$$\frac{2}{3}\frac{n^2+2}{n^2-1}=2325\cdot 29-18\cdot 541\times 10^{-8}\lambda^{-2}. \quad . \quad . \quad (3)$$

Reduced to the form (1) this gives

$$C_0=9\cdot 708\times 10^{27}; \quad p_0{}^2=11284\times 10^{27}. \quad . \quad . \quad (4)$$

These values are a little different from Cuthbertson's; but the latter were obtained from the range 6708 Å. to 4800 Å., while Friberg's were found from the extremes of his range. For comparative purposes it is better to use values deduced under similar conditions, and we therefore use Cuthbertson's values throughout as in the table in (2).

2. There are other physical and chemical properties which also suggest that CH_4 is different from the hydrides in this sequence. An investigation of the ionization potential of methane from this point of view has just been made by Pietsch and Wilcke *. They quote the ionization potentials of Ne, FH, OH_2, NH_3 as 21·5, (15), 13·2, and 11·1 volts respectively; while Grimm and others have put that of methane at 9·5 volts, so making it one of this sequence. On the other hand, later experimental values for methane range round 13·9 volts, and Pietsch and Wilcke give the value 14·6 volts.

Reverting to the dispersion formula (1), the frequency p_0 is, on the classical theory, a dominant natural frequency in the ultra-violet. Various attempts have been made lately † to identify p_0 with ionization potential, or in formulæ with several terms with ionization and resonance potentials, when the latter have been transformed into frequencies by the usual quantum relation. It seems more probable that p_0 is near the maximum general absorption on the ultra-violet side of the series limit, and this seems to have been confirmed for the inert gases by Cuthbertson's direct observation of absorption in this region ‡. However this may be, it is of

* E. Pietsch and G. Wilcke, *Zeit. für Phys.* xliii. p. 342 (1927).

† B. Davies, Phys. Rev. xxvi. p. 232 (1925). K. F. Herzfeld and K. L. Wolf, *Ann. der Phys.* lxxvi. p. 71 (1925). R. A. Morton and R. W. Riding, Phil. Mag. i. p. 726 (1926).

‡ C. Cuthbertson, Proc. Roy. Soc. A, cxiv. p. 650 (1927).

interest to turn the frequencies in the table (2) into potentials by the relation

$$V=1\cdot234\times10^{-4}\,p/c \text{ volts.} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Calling this the dispersion potential, and quoting from Pietsch and Wilcke for the ionization potential, we obtain the following series :—

	Ne.	FH.	OH_2.	NH_3,	CH_4.
V (dis.)	25·4	—	13·5	11·7	14·1
V (ion.)	21·5	—	13·2	11·1	14·6 ; (13·9)

There is no need to press the comparison too closely, for reasons we have given ; the general similarity of the two series is sufficiently striking to show the analogy between the phenomena.

3. We may conclude that CH_4 does not belong to the neon-like series of hydrides in table (2), and that optically at least it does not behave like a C^{4-} ion with four hydrogen nuclei. The atomic binding in the molecule may, of course, be of the homo-polar, or electron-sharing type ; but let us examine the alternative hetero-polar structure of a C^{4+} ion with four H^- ions. This has been proposed in a recent discussion of chemical valency by Niven *. Reviewing the chemical properties of this sequence, Niven argues that FH consists of F^- and H^+, but that, on the other hand, in methane the carbon atom has lost its 2_1 and 2_2 electrons to the hydrogen atoms to complete their 1_1 systems ; he also considers that OH_2 and NH_3 have the latter type of structure, but the optical and other evidence collected here shows that Ne, FH, OH_2, and NH_3 form a regular sequence, which is definitely broken at CH_4†.

The C^{4+} ion has a very small refractivity. If we neglect its direct contribution and also the interaction of the ions, then the refractivity of CH_4 should be that of four H^- ions to a first approximation. H^- should bear to helium a similar relation to that of F^- to neon. Thus if we form a table like (2), but with helium in the first place, H^- will be the other member, and we should expect the same value of the constant C_0 and a smaller value of p_0. Using Cuthbertson's

* C. D. Niven, Phil. Mag. iii. p. 1314 (1927).

† I find that this has also been advocated by J. H. de Boer and A. E. van Arkel, *Zeit. fur Phys.* xli. p. 27 (1927).

constants for helium, and dividing the constant C_0 for methane by four, we obtain the following table :—

Gas.	$C_0 \times 10^{-27}$.	$p_0^2 \times 10^{-27}$.
He	2·4248	34992
$\frac{1}{4}CH_4$	2·5138	11689

. . . (6)

These results agree with the view taken of the structure of CH_4, though no doubt the agreement may possibly prove to be only a coincidence. We have neglected the mutual interaction of the H^- ions ; this may be justified for the present comparative use by assuming a tetrahedral structure and using the relevant formulæ given in a previous paper *, so verifying that the effect is relatively small in this case. Just as in table (2), we were not dealing with free ions, but with ions F^-, O^{--}, and so on, under the influence of hydrogen nuclei, so in CH_4 we have H^- ions under the deforming or contracting influence of a central C^{4+} ion. In a recent paper †, Pauling has given theoretical estimates of the molecular refractivities of hypothetical free ions ; his value for H^- is 25·65, and those for F^-, O^{2-}, N^{3-}, and C^{4-} are 2·65, 9·88, 72·6, and 5400 respectively. These give, for instance, a value of 29·6 for CO_3^{--} instead of the value 12·3 assigned by Fajans and Joos ; the diminution may be attributed to the influence of the central C^{4+} ion if Pauling's theoretical values are accepted.

Again, the molecular refractivities of OH_2 and NH_3 are 3·7 and 5·5 respectively ; these may be compared with the theoretical values 9·88 and 72·6 for the corresponding free ions.

On the present view of the constitution of CH_4, we deduce a molecular refractivity of 1·61 for H^- in this combination with C^{4+} as the central ion ; Pauling's value for the free ion is 25·65.

4. The argument of this note is that a comparison of approximate dispersion formulæ for Ne, FH, OH_2, NH_3 CH_4 shows that CH_4 does not belong to this sequence, and that its molecule is not equivalent to a C^{4-} ion with four hydrogen nuclei. A similar conclusion may be drawn from the ionization potentials of this series and from other relevant data. It is shown further that the dispersion formula is not inconsistent with a molecular structure of a C^{4+} ion with four H^- ions.

* Phil. Mag. iii. p. 444 (1927).

† L. Pauling, Proc. Roy. Soc. A. cxiv. p. 181 (1927).

LXIV. *The Characteristics of Gasfilled Photoelectric Cells.* —II. *By* N. R. Campbell. (Communication from the Staff of the Research Laboratories of the General Electric Company, Ltd., Wembley.)

Summary.

The theory offered in a previous paper for the "unstable characteristic" of a gasfilled photoelectric cell was false. A new theory is outlined based on the well-studied intermittent "flashing" of neon lamps and similar discharge-tubes. It is shown that the main features of the "characteristic" accord with the ideas derived from this study, and that the complicating factors to which Taylor (with his associates) and Penning have directed attention are more important in the photoelectric cell than in the neon lamp.

Some basis is thus offered for the methods of using the cells described in another recent paper; the correction of the theory does not affect their utility. But minor corrections and improvements of the methods are described.

General Theory of the "Unstable Characteristic."

In two recent papers* attention was called to (*a*) the "unstable portion of the characteristic" of a gasfilled discharge-tube, and (*b*) its use in the detection of illumination. The object of this paper is two-fold; to correct the false interpretation of the facts that was given in the earlier of these papers, and to supplement the facts given in the later.

An attempt was made in (*a*) (p. 955 *et seq.*) to interpret a certain portion of the curves in fig. 6 as part of the characteristic of the cell, indicating a definite relation between the current through it and the potential between its electrodes; it was suggested that the form of the curve was an indication of the distortion of the field by the space-charge. But it was recorded that the current on this part of the curve was intermittent. This fact destroys completely the interpretation offered; it shows that the relation between the measured current and potential does not indicate a steady state of the cell; and therefore that all attempts to explain the relation in terms of distorted fields, recombination, and so on are beside the point.

Moreover, it should have been clear that the outlines of a

* N. R. Campbell, (*a*) Phil. Mag. iii. p. 945 (1927); (*b*) do. p. 1041 (1927).

correct interpretation had already been provided by the work of J. Taylor (with his associates) and others* on the intermittent discharge through neon lamps and similar vessels. Such vessels are characterized by an upper critical voltage V_s, necessary to start the discharge, and a lower critical voltage V_g, at which the discharge ceases. If they are connected in a circuit containing a source of potential greater than V_s and some device for limiting the mean current $\bar{i}$ to a value much less than that which flows in the discharge, the capacity C between the electrodes will be alternately charged to V_s by the external circuit and discharged almost instantaneously to V_g by the discharge. A voltmeter across the electrodes will read some value $\bar{V}$, intermediate between V_s and V^g; n, the frequency of intermittence, will be given by

$$n = \frac{\bar{i}}{C(V_s - V_g)} \quad \dots\dots \quad (1)$$

The gasfilled photoelectric cell is similarly characterized by upper and lower critical voltages; accordingly the voltage read on the voltmeter in the experiments of the previous papers should be $\bar{V}$, determined by the alternating charge and discharge of the condenser formed by the electrodes and their connexions.

According to this simple theory, $\bar{V}$ should be independent of $\bar{i}$. The characteristics given in fig. 6 of paper (*a*) have a portion PQ in which V is nearly independent of i and lies between V_s and V_g. Let us suppose that this portion represents the conditions in which the simple theory is nearly true, and let us endeavour to explain the remainder of the characteristic by the introduction of the complicating factors to which Taylor and Penning (*loc. cit.*) have drawn attention.

The facts given have reference to a cell of the "spherical" type, but not that to which fig. 6 refers. Its diameter was greater, namely 10 cm.

The Portion QR.

One of these factors enters if $\bar{i}$ is comparable with the current flowing in the discharge. If $I = f(V)$ is the relation between the current and voltage of the discharge, the current discharging the condenser is $I - \bar{i}$. As $\bar{i}$ increases, V will tend to linger in the neighbourhood of the lower values

* See *e.g.* J. Taylor and L. A. Sayce, Phil. Mag. l. p. 985 (1925); F. M. Penning, *Phys. Zeit.* xxvii. p. 187 (1926). Most of the earlier literature is cited in these papers.

for which I is small. Accordingly $\bar{V}$ will decrease as $\bar{i}$ increases, until, when $\bar{i}=I_g$, V will be constant and $\bar{V}=V_g$. On these considerations we may explain generally the portion of the characteristic QR, terminating in the steady discharge at R, where $V=V_g$. Along RS $i > I_g$, and $\bar{V}$ is the steady potential given by $\bar{i}=f(V)$.

The Portion XP.

Along XP the current is always small compared with I; the variation of $\bar{V}$ with $\bar{i}$ must be due to some influence of $\bar{i}$ upon the recharging of the condenser. Taylor and Penning have shown that, after the discharge ceases, ions and electrons are still left in the vessel; they represent the space-charge that has enabled the discharge to continue at potentials less than V_s. They will increase by some amount q_1 the quantity of electricity that has to be supplied by the external circuit in recharging the condenser, and will make it necessary to write in place of (1),

$$n=\frac{\bar{i}}{C(V_s-V_g)+q_1}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

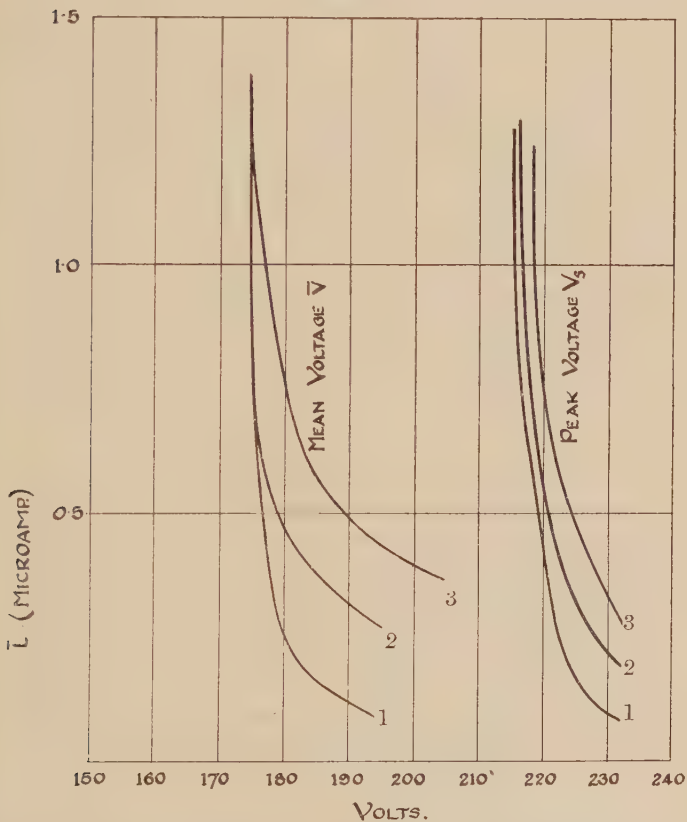
The number and distribution of the charges left can hardly depend on $\bar{i}$, so long as it is small compared with I; and if they are completely removed before the discharge starts again, q_1 must be independent of $\bar{i}$, and no reason is apparent why $\bar{V}$ should vary with $\bar{i}$. But some measurements of Penning (Table I. *loc. cit.*) indicate that, as $\bar{i}$ is increased, V_s falls; the change in $\bar{V}$ may be due to a change in V_s due to the incomplete removal of the space-charge from the previous discharge.

To examine this explanation, the maximum potential difference between the electrodes was measured with a peak voltmeter in the conditions prevailing along the portion XP; this maximum may be identified with V_s. In fig. 1 both V_s and $\bar{V}$ are plotted against i. The curves 1 refer to the cell in the dark, curves 2 and 3 to the cell under a smaller and a larger illumination. An attempt was also made to measure the minimum potential between the electrodes, but it is much less sharply defined. It was about 82 volts, and no evidence could be found that it varied with $\bar{i}$ or with the illumination. This value is much less than V_g, measured statically, which is 145 volts; the difference is due, of course, to the residual space-charge.

The changes in V, whether due to changes in i or in the

illumination, are always accompanied by changes of the same sign in V_s. There is, therefore, some evidence for the explanation offered. It is impossible to decide whether the observed changes in V_s are sufficient to account for those in $\bar{V}$ without knowing the relation between V and the time

Fig. 1.



during the whole period of charge and discharge. But since the changes in $\bar{V}$ are always greater than those in V_s, it would seem that a decrease in V_s must be accompanied by an increase of the proportion of the whole period during which V is in the neighbourhood of its lower limit. Considerations presented later indicate that such an increase is not unreasonable.

But it remains to be explained why V_s should vary with $\bar{i}$ or with the illumination. The increase with i may be due

to the decrease in the period of recharging, which may be too short for the residual charges to be removed completely; if the positive ions have been brought into the neighbourhood of the cathode, but have not been discharged by it, they will increase the field in its neighbourhood and thus decrease the starting potential. The increase of V_s with illumination would then be due to the more rapid neutralization of these positive ions by electrons emitted from the cathode; illuminations would be equivalent to an increase in the period of recharging. (Actually the whole period increases with the illumination, as is explained below.) But there is some difficulty in accepting this explanation as sufficient, because the period of recharge is so long (at least 0·01 sec.) that it should always be sufficient for the passage of the charges to the electrodes under the action of the field. Even if the secondary ionization produced by their passage is taken into account, it is difficult to prolong the period during which the residual charge may be expected to remain, so that it becomes great enough to produce the observed changes. Perhaps some kind of "polarization," such as Taylor * introduces to explain some of his results, may be present; the positive ions may arrive in the neighbourhood of the cathode, but not be discharged immediately.

The Frequency of Intermittence.

If the considerations presented are sufficient to explain the main features of the curves in fig. 6 of (*a*), they provide a theoretical basis for the "second method" of using the cells described in (*b*). We have now to consider the "third method," in which changes in n, not in V, are employed.

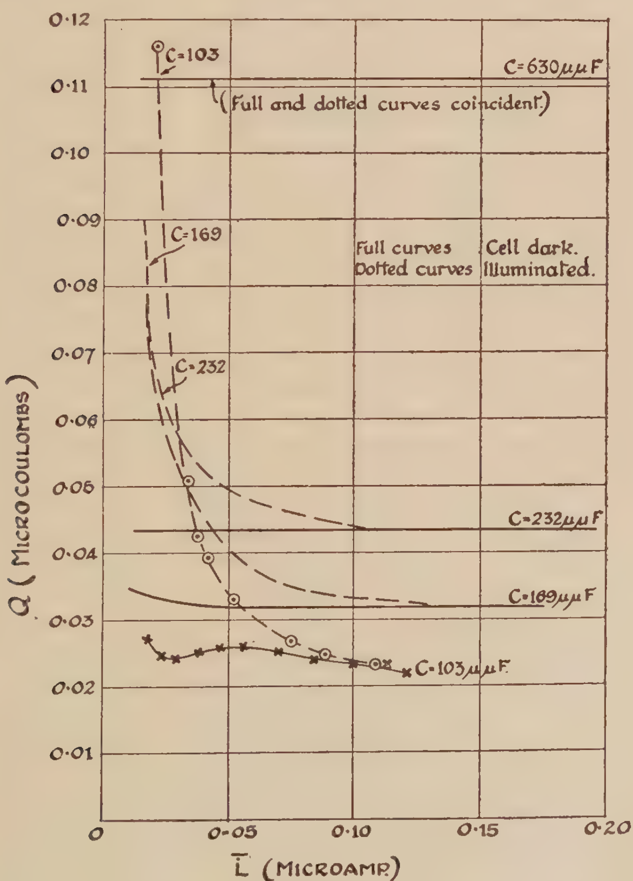
The changes in $\overline{V}$ discussed in the preceding paragraph are accompanied by changes of n, which, of course, increases with $\overline{i}$. According to (2), even if q_1 is constant, n should not be strictly proportional to i, because of the variation in V_s, but in this region no departure from proportionality could be established. n also varies with the illumination, decreasing as the illumination is increased. This change is doubtless partly due to the increase in V_s produced by the illumination; but there must be another cause which becomes more evident when smaller values of i than those shown in fig. 1 are investigated.

If $\overline{i}$ is reduced beyond the lowest value shown, n becomes so small that the voltmeter oscillates and there is no steady $\overline{V}$. At the same time it becomes difficult to determine V_s with the peak voltmeter on account of imperfect insulation. Accordingly, the curves cannot be extended further, but

* J. Taylor, Phil. Mag. iii. p. 753 (1927).

static measurements of the constant potential required to start the discharge show that V_s does not increase appreciably beyond the greatest value shown; the curve for V_s must bend sharply down and become nearly vertical. In this region, which is that to which the "third method" is applicable, changes in n cannot be due to changes in V_s, and it is improbable that they are due to changes in V_g. Some other factor must enter.

Fig. 2.



The facts in this region are best stated in terms of the quantity $\bar{i}/n$; according to the general ideas we are discussing, this must be Q, the quantity of electricity passing in each cycle, consisting of a charge and discharge of the condenser C, whatever are the processes occurring during that cycle. Fig. 2 shows Q plotted against i for various values

of the capacity C. The points are inserted on the least regular of the curves to indicate the accuracy of the measurements. The full lines refer to the cell in the dark, the dotted lines to the cell subject to a small illumination, namely that due to a source of 1 candle-power at a temperature of 2600° K. at about 100 metres distance.

In the dark, Q is nearly independent of i. It is quite indedendent when C is large, but increases slightly when both $\bar{i}$ and C are small. The maximum of Q for $\bar{i}=0{\cdot}06$ when C=103 is real; but it does not occur in all cells which show the other features, and it may be neglected in our general survey. If C is reduced further, the ticks in the telephone become very weak and irregular, and it is impossible to obtain consistent values of n. When the cell is illuminated, Q is still independent of $\bar{i}$ for the larger values of $\bar{i}$, but increases rapidly when $\bar{i}$ is small, the increase being the greater, the less is C. At the smallest values of $\bar{i}$, Q depends on $\bar{i}$ rather than on C, and is actually rather greater for the smaller capacity. The dark curves must be regarded as corresponding, not to complete darkness, but to some very small illumination. For it is well known that, even when every precaution is taken to exclude light, gasfilled cells always give a small "dark current," which behaves exactly like that due to a small illumination. In the cell to which fig. 2 refers, this dark current was unusually small; other cells, in which it is larger, gave "dark curves" similar in shape to those characteristic of illumination. It is therefore probably legitimate to conclude that, if the dark current were wholly absent, all abnormalities and irregularities would vanish, and Q would be independent of $\bar{i}$ throughout the range shown.

An outline of an explanation of these facts can be obtained by considering another complication of the simple theory, to which Taylor has drawn attention. In order that the discharge may pass, a space-charge has to be developed in the gas. During its establishment a quantity of electricity, q_2, must pass through the vessel, which is not necessarily equal to q_1, the quantity which has to pass in order to remove the space-charge when the discharge ceases. This quantity may be drawn either from the charge contained in the condenser or from the external circuit. If it is drawn from the condenser, there must be a minimum capacity C which enables the discharge to pass. For though q_2 may vary with the capacity, there must presumably be a minimum value $q_{\text{min.}}$, determined by the configuration of the electrodes, beyond

which q_2 cannot fall, however small is C. But if

$$q_{\text{min.}} > C(V_s - V_g),$$

the difference of potential across the condenser will have fallen below the value at which the discharge can be maintained before the discharge starts; in such circumstances it could never start. If the discharge is to start at all, q_2 must be drawn from the external circuit.

If q_2 were independent of $\bar{i}$, Q would still be independent of it. But there is reason to believe that it is not independent when the cell is illuminated. For if the cell is illuminated, there is always a finite current i_0, namely the greatest current that can be obtained on the Townsend characteristic, which will pass without any occurrence of a discharge. If $\bar{i} < i_0$, the space-charge, on which the discharge depends, will never develop. It is likely that if $\bar{i}$ exceeds i_0 but slightly, the current effective in establishing the space-charge will be $\bar{i} - i_0$ rather than $\bar{i}$. If we imagine that this effective current has to supply the quantity q_2, the period τ during which it flows will be $q_2/(\bar{i} - i_0)$, and the total quantity of electricity supplied during this period will be

$$q_2' = q_2 \cdot \frac{\bar{i}}{\bar{i} - i_0} \quad \ldots \ldots \ldots \quad (3)$$

Q will then be given by

$$Q = C(V_s - V_g) + q_1 + q_2',$$

and will increase as $\bar{i}$ diminishes.

According to this theory, for a given illumination the value of $\bar{i}$ at which the dotted curves begin to depart from the full curve in fig. 2 ought to be of the same order as i_0 and nearly independent of C, so long as it is below a certain limit. The second of these expectations is fulfilled. It is difficult to determine the least value of $\bar{i}$ at which the departure begins; but once it begins, the point of departure does not vary greatly with C. But the first is not fulfilled. If i_0 is determined experimentally by raising the potential across the cell and noting the value of i just before the discharge begins, then, in the circumstances of fig. 2, it is certainly 1000 times less than the critical value of $\bar{i}$; the maximum Townsend current for this illumination was far below the least which the galvanometer would indicate. But this difficulty is not insuperable. The smaller the illumination, the steeper is the upper end of the Townsend

characteristic; it is possible that the greatest current obtainable without formal instability, when the illumination is very small, exceeds very greatly any that can be actually observed.

It is not pretended that these considerations clear up the whole matter completely; they are merely intended to indicate the physical processes upon which any explanation must be based. A complete theory would require an exact understanding of the immensely complicated changes involved in the electric discharge. It is possible that further experiments along these lines would throw light on that interesting and important problem; but the work on the neon lamp, the ideas from which are the basis of this discussion, has shown how difficult it is to interpret completely any of the measurements. An illustration of this difficulty may be given from fig. 2. According to the theory, the value of Q where it is independent of $\bar{i}$ should be given by (3), if for q_2' is substituted the constant quantity q_2. The variation of Q with C ought therefore to give the values of q_1+q_2 and of (V_s-V_g). From fig. 2 we find

$$V_s-V_g = 172 \text{ volts}; \qquad q_1+q_2 = 0{\cdot}0034 \text{ microcoulomb.}$$

The value of V_s-V_g determined by means of the peak voltmeter potential was 150 volts; but this value is too great, as it assumes $q_1=0$. The value determined statically was 87 volts. Both these values are much smaller than that given by (3), and extension of the measurements to greater values of C shows that (3) is not accurately true, until C becomes of the order of $10^5\ \mu\mu$ F. Either q_1 or q_2 must vary with the capacity, and any simple interpretation of the measurements leads to serious error.

Practical Results.

The primary object of the investigation was, of course, to provide some theoretical basis for the methods of using gasfilled cells described in paper (*b*); it was hoped that they might be made less empirical. This object has not been achieved; but some corrections to the description of the third method are necessary.

First, it is not desirable (as suggested) to reduce the capacity of the insulated electrode to a minimum. If the capacity is too small (as stated above), the ticks are irregular. The capacity should be the least that gives regular ticks. If the cell is one which gives considerable dark current, this will also be the capacity for which n is a

maximum for a small value of $\bar{i}$ in the dark. The cell of fig. 2 is exceptional in this matter, since it gives a hardly appreciable dark current. The adjustment of the capacity is not at all critical, and may easily be made by means of a small variable air condenser, such as is used in wireless sets; this condenser should be inserted across the telephones and the cell in series.

Second, the constancy of N_0-N, shown in fig. 4 of (*b*), is not general. It is quite definite with the particular cell and the particular capacity used in obtaining those measurements; but in general N_0-N for a given illumination decreases somewhat as N_0 increases, It is not difficult to control N_0 with a rheostat so that it is approximately constant and N_0-N may be taken as a measure of I; but it is best, if possible, to use the method merely to determine the equality of two illuminations by means of the equality of N.

These corrections do not affect the utility of the method; further use of it confirms the impression that it is unrivalled in convenience when very small illuminations have to be measured.

A modification of it may be mentioned, suitable for illuminations within the range to which the "second method" is suitable. It consists in determining the least current $\bar{i}$ for which any ticks are obtained. If a good thermionic valve and a good rheostat are employed, it is possible to identify illuminations of the order of 1 candle at 5 metres within 5 per cent. by the position of the slider on the rheostat at which the ticks just vanish. The method is therefore rapid and, like the third method, requires no delicate apparatus.

LXV. *Modified and Unmodified Scattered X-Rays. (J-Phenomenon.*—Part VII.) *By* Prof. C. G. Barkla, *F.R.S., and* Dr. S. R. Khastgir, *University of Edinburgh* *.

IN earlier papers we gave a statement of some of the laws governing the production of the modified scattered X-radiation when the primary radiation used was heterogeneous, and the radiations were compared by absorption methods. These laws were contrasted with those obtained by A. H. Compton and others from the study of comparatively homogeneous beams by the crystal diffraction method. The laws were shown to be entirely different from those

* Communicated by the Authors.

governing, or at any rate from those said to govern the Compton effect,—they were simply the laws of the J-phenomenon. In particular, the scattered radiation may be either unmodified or modified as measured by its absorbability in one substance, say aluminium ; the change from one to the other is abrupt and it depends upon factors which had previously been considered of little or no importance in their influence on the properties of radiations. More remarkable still the radiation which, when measured in one absorbing substance is a modified radiation, is when its absorbability is measured in another substance, very clearly and precisely an unmodified radiation. In this case the modified and the unmodified radiations are one and the same ; only the testing substance is changed. We have illustrated this in a number of ways. There is no haziness about the experimental results; they leave no room for ambiguity.

The evidence of modification as we have observed it, depends upon a relation between the radiation and the testing substance. Such a fact is not provided for by either the classical or the quantum theory ; but we have seen in many ways that the property of a radiation depends, in part at least, upon an average quality more closely allied to temperature of the radiation as a whole, and not upon the frequency of its constituents except in so far as they contribute to the average ; also corresponding effects are produced in different substances at different average frequencies (or "temperatures") characteristic of the particular substance.

There is a further factor—possibly the large scale structure or sequence of radiations in the full stream of radiation which is involved ; for certain conditions in the radiation are essential to the change in activity at these "temperatures."

On the classical theory of course, the large scale structure of the scattered radiation is quite different from that of the primary producing it, on account of the super-position of waves from every electron in the scattering substance outside the atomic nuclei. Every wave in the primary radiation produces an irregular succession of waves forming a train of length $l(1-\cos\theta)$ from each filament of scattering substance of length l in the direction of primary propagation, where θ is the angle between that direction and the direction of propagation of the scattered radiation. It may be that this is the cause of the modification in properties produced by scattering,—that a certain continuity is necessary in the stream of radiation to enable it to attain a certain level of activity. This, however,

can for the present only be regarded as a hypothesis which seems to explain the difference between radiation and radiation. There is a fair amount of evidence in favour of this, but this will be discussed in other papers. At any rate, the modification produced by scattering may or may not be shown in its effect on the absorption in a particular substance. This we have already shown in a number of experiments. The contrast between our results and Compton's * is so marked that it is perhaps necessary to show that there is, at any rate, a close connexion between the two. This connexion, the conditional nature of X-ray phenomena, particularly those associated with quantum rules, and the dependence of what may be called classical and quantum phenomena on the substance intercepting the radiation, are shown very strikingly in the following experiment.

Experiment.

The absorbabilities of primary and scattered radiations were compared in several substances throughout a long range of frequencies of the primary radiation. As indicated before, the simplest method of comparing primary and scattered radiations is to find the ratio of the ionizations produced by the scattered and primary rays, first when those radiations are unintercepted before entering the electroscopes (ratio = S/P), and subsequently after both

* Perhaps the briefest way of emphasizing the difference between our results and Compton's is the following :—

The difference between the absorption coefficients of primary and scattered radiations is only shown (if at all) in definite well-marked steps. Thus if $\left(\frac{\mu}{\rho}\right)_2$ is the absorption coefficient of the radiation scattered at a definite angle θ, and $\left(\frac{\mu}{\rho}\right)_1$ is the absorption coefficient for the corresponding primary radiation,

$$\left(\frac{\mu}{\rho}\right)_2 - \left(\frac{\mu}{\rho}\right)_1 = 0, \text{ or } a, \text{ or } b, \text{ or } c \ldots\ldots$$

Also for different angles of scattering θ_1 and θ_2,

$$\left(\frac{\mu}{\rho}\right)_{\theta_2} - \left(\frac{\mu}{\rho}\right)_{\theta_1} = 0, \text{ or } a, \text{ or } b, \text{ or } c \text{ (frequently 0).}$$

The difference between these results and those of Compton are not only of fundamental importance by reason of their theoretical implications, but the results themselves, in certain regions, are as widely different in magnitude as they could possibly be. For instance, the difference between the primary radiation and that scattered at a small angle is very small on Compton's theory, whereas we usually find the difference to be precisely the same as that between the primary and the radiations scattered at, say, 90°.

beams have traversed the same thickness of some absorbing substance (ratio $= S'/P'$). It has been shown already that S'/P' may be equal to S/P, indicating equality of absorptions of scattered and primary beams, or S'/P' may be quite markedly less than S/P, indicating greater absorption of the scattered radiation than of the primary, *i. e.* a modified scattered radiation. The change from the unmodified scattering to the modified scattering takes place abruptly; it may, however, be brought about in many different ways.

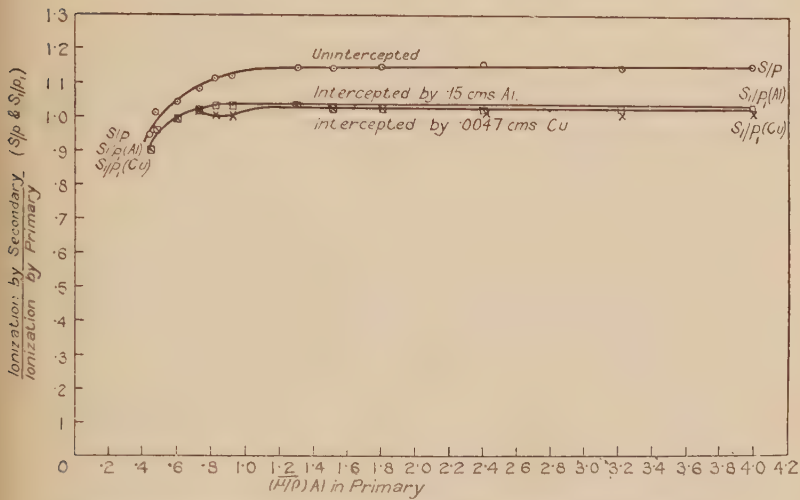
For illustration of these facts, reference should be made to previous papers. What we propose to show now is that while absolutely regular and consistent results may be obtained when the radiations are examined in some substances, two alternative results, which are themselves as widely different as the classical and quantum laws, may be obtained when these radiations are examined in other substances.

A primary beam was partially scattered by transmission through a sheet of paraffin wax as in previous experiments. The scattered radiation at right angles to the primary radiation was definitely more absorbable than the primary radiation when measured in aluminium, copper, or gold. Not only so, but the apparent transformation by scattering—the real transformation in some respects—received quite consistent evidence from the absorption measurements in these three substances. The change in scattering was just of the kind which would be produced by Compton's change of wave-length—if we ignore the relation with wave-length and with scattering angle, which are as already stated. On the other hand, while there was this satisfactory consistency between the results obtained from absorption measurements with these three substances, most striking results were obtained when silver and tin were used as absorbing substances; the interesting feature of these elements being the existence of their K-absorption edges within the limits of the spectrum of the radiation employed. The results obtained with silver and tin were not irregular, they showed a double regularity, for they were either *a* or *b*. Either is interesting, significant, and intelligible*; but the two are totally different, one following the classical laws, the other appearing to follow quantum rules. Yet an otherwise imperceptible change in the radiation determines whether the result shall be (*a*) or (*b*). This is all shown in figs. 1, 2, 3, and 5, in which the ratio of ionizations by scattered

* At least as intelligible as quantum theory.

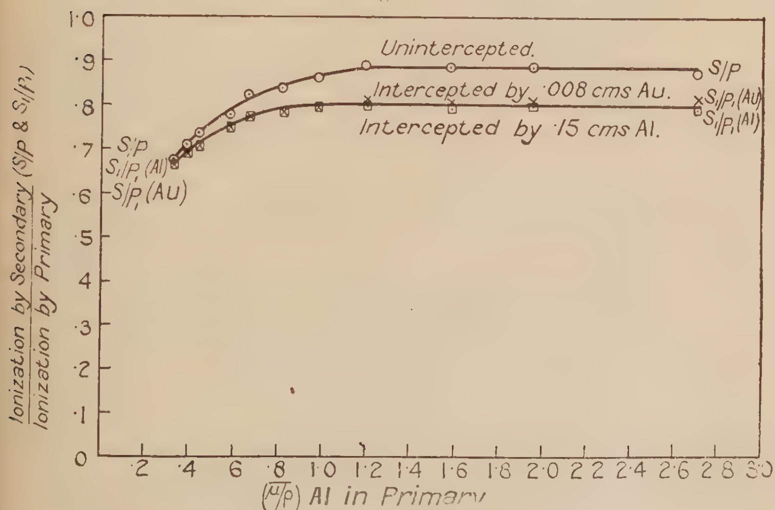
and primary radiations is plotted against the average absorption coefficient of the radiation employed $\left(\frac{\overline{\mu}}{\rho}\right)^*$.

Fig. 1.



Showing equal amounts of modification as measured in Al and Cu.

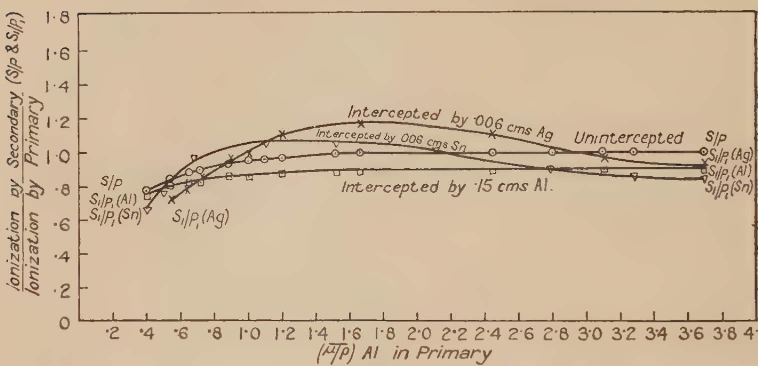
Fig. 2.



Showing equal amounts of modification as measured in Al and Au.

* Calculated as previously from a 50 per cent. diminution of ionization in a short ionization vessel.

Fig. 3.



Showing selective absorptions in Ag and Sn consistent with change in wave-length on scattering.

Proceeding from low to high frequencies (from right to left) it is seen that :—

(1) The ratio of ionizations produced by scattered and primary radiations was a constant through a long range of frequencies. This is shown by lines marked S/P which are horizontal except for high frequencies. The horizontality is shown by other experiments to extend far beyond the limits of these figures to the right; in fact beyond the value $\overline{\left(\frac{\mu}{\rho}\right)}_{Al} = 12$;

(2) when the scattered and primary radiations were transmitted through equal thicknesses of absorbing material, Al, Cu, or Au, the ratio of ionizations (S'/P') was markedly less, showing that the scattered radiation was more strongly absorbed than the primary radiation as usually measured. The values are shown on the curves S'/P' (Al), S'/P' (Cu), S'/P' (Au) in figs. 1 and 2 ;

(3) the difference between the absorption coefficients of scattered and primary radiations was a constant through a long range of wave-lengths, *i. e.* $\overline{\left(\frac{\mu}{\rho}\right)}_2 - \overline{\left(\frac{\mu}{\rho}\right)}_1 =$ constant as shown by the horizontality of lines marked S'/P'. Such results have been previously published.

(4) The fractional change (by scattering) in the absorption coefficient of a radiation of given wave-length was approximately the same in Al, Cu, and Au. This is shown by the fact that when thicknesses of Al, Cu, and Au were chosen to absorb approximately equal amounts of radiation, the ratio S′/P′ was the same for these testing substances ;

(5) the results obtained when silver and tin were used as absorbing substances were of a dual nature. In a series of experiments the absorptions in these substances varied throughout the spectrum precisely as would be expected on the assumption of a change in wave-length by scattering.

Thus (fig. 3) when the wave-length of a primary radiation was fairly long, the absorbability of the scattered radiation in silver was greater than that of the primary, in agreement with the results obtained from absorption measurements in Al, Cu, and Au. As the frequency of the primary was gradually increased, the absorption of this primary radiation in silver began to rise relative to the absorption of the corresponding scattered radiation, and continued to do so until the primary became much more absorbable than the scattered radiation. This is shown by the rise of the values of S′/P′ (Ag) in passing from right to left. It is in conformity with the theory of the greater wave-length of the scattered radiation, for as primary and scattered beams increase in frequency, the primary passes the K-absorption edge first ; consequently its absorption rises relative to the absorption of the scattered radiation. With a further increase in frequency, the scattered radiation also passed the K-absorption edge in Ag, and the absorption of scattered radiation rose relative to that of the primary, the ratio of the two absorptions becoming quite normal again as it should away from the region of a K-absorption edge.

Confirmation of this result was obtained by the use of tin as the testing substance, as the K-absorption edge for tin is of higher frequency than that for silver. In this case as the frequency was increased the rise in the absorption of the primary radiation relative to that of the secondary occurred when the radiation was of higher frequency than that showing the corresponding phenomenon in silver (fig. 3). Also the rise in the absorption of the scattered radiation occurred at a correspondingly higher frequency.

All these results must be recognized as overwhelming evidence that the difference of absorbability between the

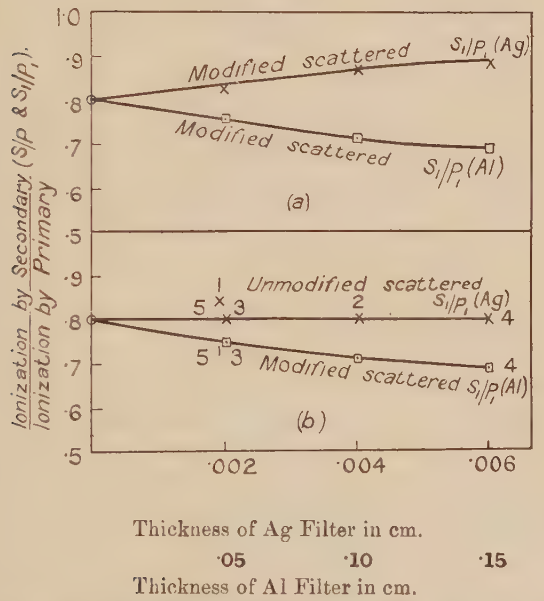
primary and scattered radiation which we observed in these experiments (and many others) was the accompaniment of Compton's "increase in wave-length" by scattering, for the increase in absorbability measured in these various substances was in the proportion expected if due to increase in wave-length; and there was shown even the selective variation in the absorptions of primary and scattered radiations such as would be expected in the neighbourhood of absorption edges in the absorbing substances. It is important to point out, too, that these results were obtained consistently, time after time, in a long series of experiments.

But while experimenting on the absorption of scattered and primary radiations by successive sheets of silver, all evidence of modification by scattering suddenly disappeared, and the scattered radiation became unmodified scattered radiation as far as its relation to silver was concerned: and this new state of things persisted*. On re-examining the absorptions in aluminium however, the scattered radiation was still a modified radiation. Thus fig. 4 shows the ratio S/P for unintercepted beams and S′/P′ for various thicknesses of aluminium and of silver placed in the path of both primary and secondary beams. In fig. 4 *a* the fall of S′/P′ (Al) with increasing thickness of intercepting aluminium, and the rise of S/P′ (Ag) with increasing thickness of silver, show the greater absorbability of the scattered radiation in aluminium, and the smaller absorbability in silver compared with the corresponding absorptions of the primary radiation. This is explained above, as the radiation experimented upon was in the neighbourhood of the K-absorption edge in silver. On repeating the experiment (with a thin sheet of Al in the primary beam before falling on the scattering substance) exactly similar results were obtained in aluminium; silver, too, commenced to give exactly the same results as before, but after filtering by the first sheet of silver (·002 cm. thick) the sudden change was observed as indicated in fig. 4 *b*. (The numbers on the figure indicate the sequence of the observations.) The difference between the absorptions of primary and scattered radiations in silver had abruptly disappeared, and did not return on re-determining the ratio for one sheet of silver. This is shown by the horizontal line S′/P′ (Ag) in fig. 4 *b*, obtained subsequent to the point marked (1) which was the same as in fig. 4 *a*.

* In all the experiments described in this paper the radiation was generated in a Coolidge tube excited by an induction coil with mercury-jet interrupter.

This compelled us to return to a comparison of the scattered and primary radiations through a long range of frequencies as in the experiments, the results of which are recorded in figs. 1, 2, and 3. In order to avoid all possible effects of even a slight variation in the radiation used, the absorptions in aluminium and silver were taken alternately throughout the whole investigation. The experiments with Al as the absorbing substance showed that the scattered radiation was still a modified radiation, modified by exactly the same

Fig. 4.



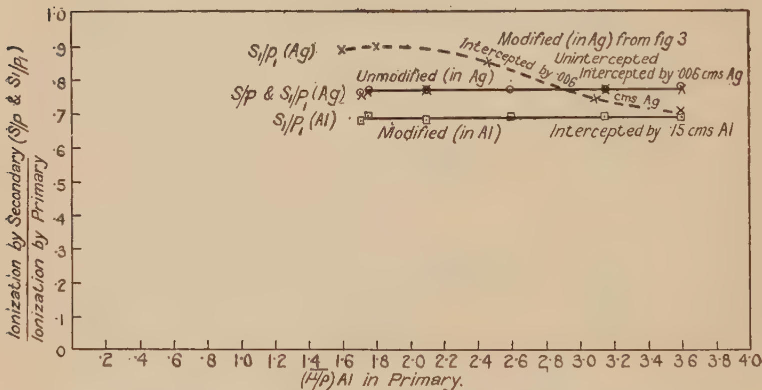
Showing how a scattered radiation which was found to be modified when examined in Al and Ag (fig. 4 *a*) suddenly became unmodified when again examined in Ag, but remained modified as examined in Al (fig. 4 *b*).

amount as in the many previous experiments: thus S′/P′ (Al) is below S/P in fig. 5. But when the scattered and primary radiations were absorbed by Ag, all difference between them disappeared—S′/P′ (Ag) was precisely equal to S/P. The two are superposed in fig. 5. In order to show the change which had occurred in the absorptions in Ag, the curve S′/P′ (Ag) is introduced from fig. 3 in broken line. Thus aluminium absorptions showed no variation from the

modified scattered radiation, whereas silver absorptions showed a complete change from the results of fig. 3 following the quantum rules to those obeying the classical laws.

This is in perfect harmony with our previous statements regarding the J-phenomenon. We have shown that a scattered radiation which is a modified radiation when intercepted by one substance is an unmodified radiation when intercepted by another substance; in this paper, however, it is shown to hold throughout the whole spectrum experimented upon, *i. e.* from low frequencies to high frequencies even including the K-absorption edge of the absorbing substance.

Fig. 5.



Showing scattered radiation, which is modified when intercepted by Al, and is totally unmodified when intercepted by Ag, for radiations of different frequencies. Dotted line shows how under other conditions Ag may show modification by scattering.

These experiments thus show in a much more convincing way what we have already demonstrated over very limited regions, that the evidence of transformation of a radiation by scattering, depends upon a relationship between the scattered radiation and the material used to test the radiation.

In any one substance the modified and the unmodified scattered radiations are alternative results obtained when there is not the slightest indication of variation in other substances. But more important still, the unmodified and the modified scattered radiations as measured in different substances frequently are one and the same radiation unless a radiation may be regarded as changed when the substance placed in its path is changed.

Summary.

The experiments described in this paper show that the scattered radiation, which is quite consistently a modified scattered radiation as measured by its absorption in a number of substances, may be either a modified radiation or an unmodified radiation when its absorbability is measured in another substance. This has been demonstrated throughout a long range of frequencies including absorption edges in the testing substances.

Thus the unmodified scattered radiation (classical theory) and the modified scattered radiation (quantum rules) in certain circumstances are one and the same radiation, the evidence of modification being dependent upon a relationship between the radiation tested and the testing substance.

This is in harmony with what we have previously stated of the laws governing the J-phenomenon.

The results are entirely at variance with a conception of independent quanta, and illustrate the importance of what we have called "temperature" of the radiation, and upon some other factor, possibly the large-scale structure of the radiation upon which the coherence of that radiation depends.

The authors wish to express their thanks to Mr. W. H. Stevens for his assistance in the experimental work described in this paper.

LXVI. *A Vacuum Spectrograph and its Use in the Long X-Ray Region.* *By* J. SHEARER, *B.A., M.Sc., Evening Lecturer in Natural Philosophy in the University of Melbourne* *.

[Plate XVII.]

THE first extensive measurements of X-ray wave-lengths were made in 1913 by Moseley †, who adopted the crystal reflexion method and photograph recording. He found that the absorption, even in hydrogen, of waves longer than 3 Å. was so great as to make a vacuum spectrometer necessary. With it Moseley ‡ measured wave-lengths up to 8 Å. Absorption in the window separating the X-ray tube from the spectrograph becomes increasingly difficult to surmount for waves longer than 10 Å., although celluloid windows have been used § for wave-lengths as long as 18 Å. in the L series of iron.

* Communicated by Prof. T. H. Laby, D.Sc.

† Moseley, Phil Mag. xxvi. p. 1020 (1913).

‡ Moseley, Phil. Mag. xxvii. p. 703 (1914).

§ Siegbahn & Thoræus, *Ark. f. Mat. Astr. o. Fys.* xviii. no. 24 (1924).

Preliminary results were obtained by Thoræus and Siegbahn * with a spectrograph designed without a window. Using a palmitic acid crystal ($2d = 71{\cdot}19$ Å.), they extended the L series to chromium (LαCr $= 21{\cdot}69$ Å.).

Redeterminations of values for the elements from zinc to chromium have been made by Thoræus †, who used two types of X-ray tube. In one, a thin wall between cathode and anode perforated by small holes and covered with aluminium foil prevented both a deposit on the anode of tungsten from the filament and also, in the absence of a window, the entrance into the spectrograph of light from the cathode. In the other, a window was used over the slit which served also as anode. The lines Thoræus obtained were very diffuse, being about 2·5 mm. wide.

Later in the same year Thoræus ‡ announces the measurement of the oxygen Kα (23·73 Å.) and the vanadium Lα (24·2 Å.) lines.

Dauvillier § claims to have bridged the spectral gap from 20 Å. to Millikan's optical limit ‖ of 136 Å. He used as crystal a film of melissic acid on lead which behaves as a crystalline body of grating space 87 Å. ¶ A thin deposit of magnesium on a celluloid film 10^{-5} centimetre thick constituted the window. In the K series ** the Kα line of oxygen (24·8 Å.), carbon (45·5 Å.), and boron (73·5 Å.) have been measured. No extensions were made to the L and M series, but the N and O series of barium were traced to 71·5 Å., and the same series of thorium to 121 Å.†

Thoræus †† criticises these results on the ground that, in view of the very strong absorption he found for wave-lengths greater than 13 Å., there is not sufficient evidence that Dauvillier's lines do not arise from reflexion in higher orders or from other atomic planes. The interpretation given by Dauvillier is rendered more doubtful by the fact that he observed optical reflexion ** in this region. Until

* Thoræus & Siegbahn. *Ark. f. Mat. Astr. o. Fys.* xix. A, no. 12 (1925).

† Thoræus, Phil Mag. i. p. 312 (1926).

‡ Thoræus, Phil. Mag. ii. p. 1007 (1926).

§ Dauvillier, *C. R.* clxxxiii. p. 656 (1927).

‖ Millikan, Proc. Nat. Acad. Sci. vii. p. 289 (1921); Astr. Journ. liii. p. 150 (1921).

¶ Trillat, *Ann. de Phys.* vi. p. 5 (1926); Dauvillier, *C. R.* clxxxii. p. 1083 (1926).

** Dauvillier, *C. R.* clxxxiii. p. 193 (1926); *Journ. de Phys. et le Rad.* viii. p. 1 (1927).

†† Thoræus, 'Nature,' cxviii. p. 771 (1926).

the K, L, and M spectra of the elements are extended systematically to the elements of low atomic number instead of at random, the interpretation of results in this region will be open to some doubt. The author's own experiments fail to show, with an alternating potential of 240 volts (340 volts maximum) applied to the tube, any photographic action, through 10^{-4} cm. of aluminium foil, on Schumann film placed in the direct beam passing through the slits. Exposures up to 300 milliamp. minutes were used. The shortest waves present would be 36 Å. long.

Before describing a windowless X-ray spectrograph, certain results obtained which disagree with those previously reported for the wave-length of Ni $L\alpha$ and for the grating space of a sugar crystal will be given.

When the author began the experiments outlined in this paper, no spectrograph had been designed that would permit of the elimination of the window by employing the common vacuum in the X-ray tube and spectrograph. With such a spectrograph (described below) the author has photographed the $L\alpha$ line of nickel on Eastman X-ray film (Superspeed) with an exposure of three hours, using a sugar crystal. The line is somewhat diffuse, having a breadth of nearly 0·5 mm., but is considerably sharper than has been observed in work previously published. The following values were obtained from the relation $n\lambda = 2d \sin\theta$, where d = crystal constant and θ = grazing angle :—

Nickel $L\alpha$.

Film.	λ (in Å.).
1	14·5709
2	14·5753
3	14·5747
4	14·5625
5	14·5764
Mean... ...	14·5720

Average Residual = 0·0042 Å. Thoræus's value is 14·528 Å.

A method of measuring θ with precision from a single exposure was adopted. It is described at the end of the paper. These measurements of λ were made relative to d = 3029·04 X units for calcite by the following procedure.

In the first place, wave-lengths of the components of the K Niα doublet were measured in the first- and second-order spectra, a calcite crystal (d = 3029·04 X.U.) being used

and the double exposure method. The following are the values :—

Nickel Kα doublet.

Film.	Order.	Kα_1 (X units).	Kα_2 (X units).
6	1	1654·02	1658·23
	2	1654·20	1658·05
7	1	1653·92	1658·20
	2	1654·43	1658·42
8	1	1653·65	1657·97
	2	1654·10	1657·94
9	1	1653·82	1658·00
	2	1654·06	1657·88
	Means..................	1654·03	1658·09
	Average Residual ...	0·17	0·15

In the double-exposure method a rotation of the crystal through $(\pi - 2\theta)$, where θ is the grazing angle for the particular line, and of the film through 4θ, would bring the two exposures of the given line into exact super-position. It is an advantage to have the two exposures separated by a small amount (of the order of 1 mm. or less) and to convert this displacement on the film into angular measure. For all exposures the film was held in a holder which bent it into an arc of exactly 10 cm. radius of curvature, and was accurately set at a distance of 10 cm. from the axis of the rotation of the crystal. From the linear displacement of the two lines on the film, therefore, the corresponding angle could be computed. This displacement was measured by a projection method which will be subsequently described in another paper from this laboratory. The lines on the film are curved. When the actual rotation of the film is less than 4θ (as was always the case with these films) the lines are convex to one another and the minimum distance apart is measured. Each film was measured five times. The maximum range in the measurements corresponds to an error of 0·2 X unit, the average residual to an error of 0·02 X unit, which is less than one-fifth the error in the final values of λ.

In all crystal settings the crystal face could be set in the rotation axis with a maximum error of about 0·005 mm., corresponding to an error in λ of 0·3 X unit in the first order and 0·2 X unit in the second order. No systematic error in the results is found which would be accounted for by an error in the position of the crystal face.

Next, the spacing of cane-sugar was determined in terms of the above values of the wave-lengths of $K\alpha_1$ and $K\alpha_2$ of nickel, the third- and fifth-order spectra being used.

Grating space for Sugar (100 face).

Film.	Reference line.	Order.	Spacing (2*d*).
10	$K\alpha_1\alpha_2$	3	21·1602 Å.
	$K\alpha_1$	5	21·1492
	$K\alpha_2$	5	21·1511
11	$K\alpha_1\alpha_2$	3	21·1909
	$K\alpha_1$	5	21·1501
	$K\alpha_2$	5	21·1449
12	$K\alpha_1\alpha_2$	3	21·1343
13	$K\alpha_1\alpha_2$	3	21·1743
		Mean	21·1519
		Average Residual...	0·0077

Excluding the last two films reduces the Average Residual to 0·0031 Å.; the mean value of $2d$ is hardly affected. Stenström's* value is 21·141 Å. The lower precision in the determination of the sugar constant compared with that attained in the $K\alpha$ wave-length determination is due to the inferiority for X-ray spectroscopy of the sugar crystal and its small dispersion.

In exposing for the Ni $L\alpha$ line, comparatively strong reflexions of the Ni $K\alpha$ doublet were obtained from an atomic plane approximately in the position of the $60\bar{1}$ plane. The corresponding grating space $\left(\frac{2d}{n}=2·406\,\text{Å.}\right)$ as calculated from the X-ray photographs could not be reconciled with the data of Becker and Rose †, which give $d=$ 1·749 Å.

The discrepancy is being investigated in this laboratory.

Difficulty is experienced in long X-ray wave-length measurements by the crystal reflexion method, and arises from :—

(1) Necessity of procuring a crystal with large spacing and small absorption.

* Stenström, *Diss. Lund,* 1919.

† Becker & Rose, *Zeit. f. Phys.* xiv. p. 369 (1923).

(2) Absorption in the window between spectrograph and X-ray tube.

(3) Absorption in the air between the slit and crystal and between the crystal and plate.

(4) The difficulty of obtaining a sufficiently intense source of X-rays.

(5) Absorption in the covering over the photographic plate or film.

(6) Absorption in the gelatine of the photographic film or plate.

These difficulties will be treated separately.

(1) A crystal of cane-sugar fulfils requirements for a limited extension into the spectral gap region.

(2) and (5). The window serves two purposes.

(*a*) the separation of the X-ray vacuum in the tube from the vacuum in the spectrograph ;

(*b*) the absorption of light from the cathode that would otherwise enter the spectrograph and fog a naked film.

It is desirable to employ a naked film in order to overcome absorption in a light-tight covering for the film.

(3) The absorption of soft X-rays in air necessitates the employment of a vacuum spectrograph in which the pressure is maintained at at least 0·01 mm.

Difficulties (2), (3), and (5) above were overcome by using an X-ray spectrograph which employs a common vacuum in tube and spectrograph and which permits of the rotation through known angles of the crystal and photographic film from outside the spectrograph while it is evacuated.

The instrument is described below.

(4) A water-cooled nickel target was used ; the L series of nickel lie in the spectral region which is under investi-tion. With a Wehnelt cathode the tube operated at 15,000 volts and about 10 milliamps. It is described below.

(6) Wave-lengths up to 15 Å. could be recorded on Eastman X-ray film (Superspeed). With the object of reducing the exposures necessary, Schumann (Hilger) film was also used and subsequently rejected, since the ratio of the intensity of the background of scattered radiation, fog, and pressure marks to that of the lines was greater for Schumann film, which, however, was not new film, than for the Eastman film.

This spectrograph is shown in Pl. XVII. (figs. 1 and 2). It

consists of a brass cylindrical box (A) $8\frac{1}{2}$ inches in diameter with a conical bearing of mild steel, case-hardened, let into the base. This bearing carries two concentric cones. To the lower end of the outer (hollow) cone of gun-metal is attached a Watts 6-in. theodolite circle (B) accurately centred and reading with micrometer eyepieces (C) to 5 seconds of arc, and to the upper end an arm carrying a curved film-holder (D) of 10 cm. radius of curvature. An accurate circle was used for recording the rotation of the film as the spectrograph was designed for absolute measurements of the kind which are described above. The innermost cone is solid and of mild steel, case-hardened, supporting on its upper end the crystal table (E), and to the lower end a circle (F) reading to 3 minutes of arc, and an arm (G) for rotating the crystal during exposure. The arm is held by means of a spring against a heart-shaped cam (H) driven by a small motor (I). The angle of sweep of the crystal may be varied over a wide range. The gun-metal conical bearing was carefully turned, and the inner and outer steel bearings turned, then case-hardened, and ground to fit the gun-metal bearing. Castor-oil was used as the lubricant. Either cone could be clamped ; the gun-metal one could be rotated with worm and worm-gear (J).

The cylindrical box was closed with a lid, the lower surface of which and the upper surface of the box were ground. Tap-grease in between rendered the lid quite vacuum-tight. The conical bearings when made as described were also vacuum-tight, and remained so during rotation of either cone while the spectrograph was evacuated. To maintain the vacuum, Siegbahn and Thoræus had found it necessary to make a channel around the bearing surfaces of the cones and in the flange under the lid of the spectrograph. In order to reduce leakage of air into the spectrograph, these channels were evacuated by the backing-pump.

The X-ray tube of the Coolidge type is of metal, the general design of which has been previously described in a paper from this laboratory *. It consists of a water-cooled brass tube (K) which carries at one end glass tubing (L) acting as insulator and supporting a metal plate (M), and at the other end a water-cooled Wehnelt cathode which is screwed into the metal tube and sealed, the seal being water-cooled. The water-cooled anode (of copper, nickel-plated) is hollow and is supported by two copper tubes (N) through which the cooling water flows. A front and back slit in a

* Eddy & Turner, Proc. Roy. Soc. A, cxi. p. 117 (1926).

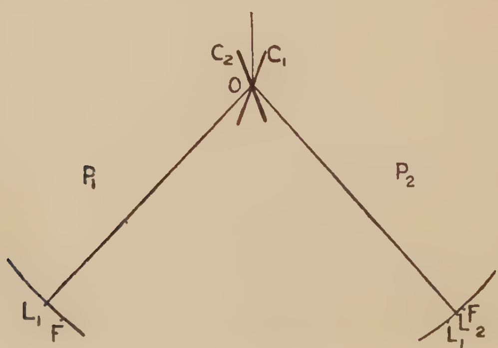
side tube fixed relative to the spectroscope necessitates the employment of an adjustable anode. This adjustment is carried out by softening the wax where the two copper tubes passed through the metal plate, and screwing the anode in or out by means of thread (O).

The use of a Wehnelt cathode reduced the light-intensity to a negligible amount. Further provision for reducing the amount of light entering the spectrograph was made by inserting in the X-ray tube opposite the side tube carrying the slits a thin sheet of copper prepared with a matt surface of copper oxide. The rest of the internal surface of the tube was silver-plated to reduce the emission of occluded gases.

Fogging due to light was absent. Scattered radiation was reduced by using a horizontal back slit that limited the length in the vertical direction of the X-ray beam incident on the crystal.

The pumping system consisted of a mercury condensation pump backed by a Cenco Hyvac (rotary oil) pump.

In order to obviate the necessity of taking two exposures when those exposures were long, a fiducial mark was made on the film. The reading of the circle attached to the film-carrier when this mark is in the plane which passes through the slit and axis of rotation of the crystal may be called the "zero reading" of the circle (Z). It was deduced from observations obtained in the double exposures made for the determination of the lattice constant of sugar which are described above. The fiducial mark is photographed on the film, simultaneously with the exposure for the lines, by the faint scattered radiation which is present during an exposure. The "zero reading" may then be determined as follows :—



R_1, R_2 = circle readings for the 1 and 2 positions P_1, P_2.
L_1, L_2 = the lines on film for the two exposures.

In position P_2,

$$d\theta = \angle L_1OL_2, \quad d\theta_1 = \angle L_1OF, \quad d\theta_2 = \angle L_2OF.$$

Now $$4\theta = R_2 - R_1 + d\theta.$$

$$\therefore \; Z = R_1 - d\theta_1 + 2\theta$$

$$= \frac{R_1 + R_2 + d\theta - 2d\theta_1}{2} \quad \text{or} \quad \frac{R_1 + R_2 - d\theta - 2d\theta_2}{2}.$$

A single exposure then suffices for measuring the grazing angle of any line and for calculating its wave-length from the relation $n\lambda = 2d \sin\theta$. As the only assumption made in determining the "zero reading" is that of the equality of the reflexion angles in each of the two symmetrical settings of crystal and film, the precision of absolute determinations of wave-lengths in the L series is not impaired.

I wish to express my gratitude to Professor Laby for the encouragement and assistance that were at all times given, and for the many fruitful suggestions made throughout the course of this work.

My thanks are also due to Miss N. Allen, M.Sc., whose interest in the problem of the crystal structure of sugar was much appreciated.

LXVII. *On the Radiation from the Inside of a Circular Cylinder.* *By* H. Buckley, *M.Sc., F.Inst.P.* (From the National Physical Laboratory*.)

In the Philosophical Magazine of July 1920, Bartlett † gives an expression for the amount of heat radiated from the inner walls of a uniformly-heated cylinder on to a coaxial circular area normal to the axis of the cylinder. The main point in his paper is the proof that the radiation from the inner walls of the cylinder between A and B on to the coaxial circular area C (fig. 1) is equal to that which it would receive from a circular disk at B, less what it would receive from a circular disk at A, both disks having the same temperature and emissivity as the walls of the cylinder.

It is due to this point of view that Bartlett's method of considering the problem is at once much simpler and much more powerful than that used by Owen ‡, who obtained the

* Communicated by Sir J. E. Petavel, K.B.E.

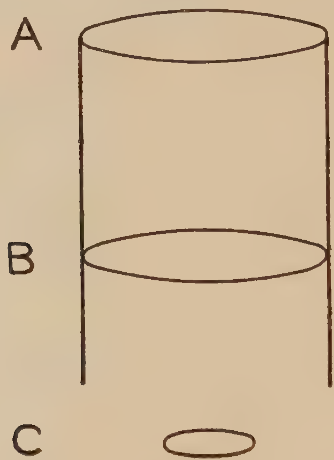
† Bartlett, Phil. Mag. xl. p. 111 (1920).

‡ Owen, Phil. Mag. xxxix. p. 359 (1920).

same results from first principles by the long and laborious process of quadruple integration over the surfaces of the disk and walls of the cylinder.

Both Bartlett and Owen neglected the occurrence of multiple reflexions between the walls of the cylinder such as would normally occur in practical problems where the emissivity of surfaces are necessarily less than unity. It is possible, however, to use Bartlett's method to calculate the effect of the multiple reflexions in building up the approximation to black-body radiation, which is obtained from the inside of a uniformly-heated cylinder.

Fig. 1.



The present paper in consequence has for its object the determination of the amount of energy radiated from points in the neighbourhood of the end of a uniformly-heated infinite cylinder, account being taken of the multiple reflexions between the cylindrical walls of the cylinder. The problem is of interest particularly in optical pyrometry, where uniformly-heated cylinders have been used as sources of black-body radiation. If such a cylinder be infinitely long, it is obvious that as near an approximation to black-body radiation corresponding to the temperature of the cylinder walls as is desired can be obtained by sighting the optical pyrometer on to a portion of the walls sufficiently far removed from the end.

In practice it is assumed that "black-body" conditions are realized; but there does not appear to be any quantitative assessment of the approximation to those conditions which is actually obtained.

The radiation received by a circular disk from a diffusely-radiating circular disk parallel and coaxial with the receiving disk is given by Walsh* as

$$\frac{\pi E}{2}\left\{(a^2+r^2+R^2)-\sqrt{(a^2+r^2+R^2)^2-4r^2R^2}\right\},$$

where E is the total radiation emitted by the radiating disk per unit area, a is the distance apart of the disks, and r and R are their radii. In the case where $r=R$ and the positions of the two disks are defined by coordinates x and x_1 measured along the line joining the centres of the disks, this expression reduces to

$$\frac{\pi E}{2}\left\{(x\sim x_1)^2+2r^2-(x\sim x_1)\sqrt{(x\sim x_1)^2+4r^2}\right\};$$

i. e., $$\frac{\pi E}{2}\left\{(x-x_1)^2+2r^2-(x-x_1)\sqrt{(x-x_1)^2+4r^2}\right\}$$

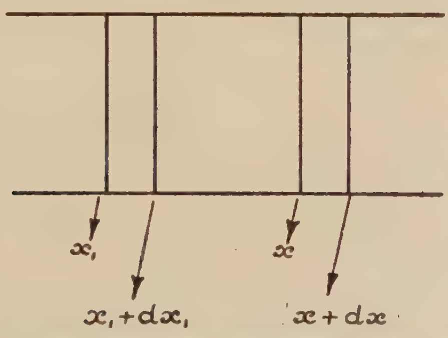
when $x>x_1$

and $$\frac{\pi E}{2}\left\{(x_1-x)^2+2r^2-(x_1-x)\sqrt{(x_1-x)^2+4r^2}\right\}$$

when $x<x_1$.

Consider now a circular cylinder (fig. 2) of radius r and

Fig. 2.



of infinite length emitting perfectly diffuse radiation of amount $\phi(x)$ per unit area at any point x measured from the end of the cylinder.

* Walsh, Proc. Phys. Soc. xxxii. p. 59 (1920). See also Sumpner, Proc. Phys. Soc. xii. p. 10 (1892).

Consider also an elementary annulus of the cylinder of width dx at x so small that the radiation emission may be regarded as sensibly constant over its surface.

Then the radiation received by a disk at x_1 from the annulus at x is given by the difference between the radiations received by the disk at x_1 from disks at x and $x+dx$;

i. e., $$-\frac{\pi}{2}\phi(x)\{f(\overline{x+dx}\sim x_1)-f(x\sim x_1)\};$$

i. e., $$-\frac{\pi}{2}\phi(x)\frac{d}{dx}f(x\sim x_1)dx,$$

where

$$f(x\sim x_1)=\{(x\sim x_1)^2+2r^2-(x\sim x_1)\sqrt{(x\sim x_1)^2+4r^2}\}.$$

Similarly, the radiation received by the elementary annulus at x_1 is given by the difference between the radiations received by disks at x_1 and x_1+dx_1 from the annulus at x;

i. e., $$-\frac{\pi}{2}\phi(x)\left\{\frac{d}{dx}f(x\sim\overline{x_1+dx_1})-\frac{d}{dx}f(x\sim x_1)\right\}dx;$$

i. e., $$-\frac{\pi}{2}\phi(x)\frac{d}{dx_1}\frac{d}{dx}f(x\sim x_1)\,dx\,dx_1.$$

Now, the area of the elementary annulus at x_1 is $2\pi r\,dx_1$. Hence the radiation received per unit area at x_1 from an annulus at x is given by

$$-\frac{\phi(x)}{4r}\frac{d^2}{dx_1\,dx}f(x\sim x_1)dx.$$

Thus the radiation per unit area received at x_1 from the whole cylinder is given by

$$-\frac{1}{4r}\int_0^\infty \phi(x)\frac{d^2}{dx_1dx}f(x\sim x_1)\,dx.$$

Writing $f(x-x_1)$ for $x>x_1$, $f(x_1-x)$ for $x<x_1$, and $-\frac{d}{dx}$ for $\frac{d}{dx_1}$ makes this equal to

$$\frac{1}{4r}\left\{\int_0^{x_1}\phi(x)\frac{d^2}{dx^2}f(x_1-x)\,dx+\int_{x_1}^\infty \phi(x)\frac{d^2}{dx^2}f(x-x_1)\,dx\right\}.$$

For the case of the cylinder in which multiple reflexions occur, if an initial distribution of radiation emission is given, the first reflected distribution may be thus obtained, and from this again the second reflected distribution and so on. The sum of the initial and the reflected distributions gives the final approximation to black-body radiation from the inside of the cylinder.

Assume the walls of the cylinder are maintained at a constant temperature T, that the walls are perfectly diffusing as before, and that the emissivity is ϵ, which is constant throughout the spectrum. Then the reflexion coefficient is $(1-\epsilon)$. Let distances be measured in terms of r, the radius of the cylinder ; *i. e.*, put $r=1$. Then $f(x)$ becomes

$$\mathrm{F}(x)=\{x^2+2-|x|\sqrt{x^2+4}\}.$$

The initial distribution of emitted radiation is $\epsilon\sigma\mathrm{T}^4=\phi_0(x)$. Then the radiation received at any point x_1 from the whole of the cylinder is given by

$$\frac{1}{4}\left\{\int_0^{x_1}\phi_0(x)\frac{d^2}{dx^2}\mathrm{F}(x_1-x)dx+\int_{x_1}^{\infty}\phi_0(x)\frac{d^2}{dx^2}\mathrm{F}(x-x_1)dx\right\},$$

so that the first reflected distribution $\Phi_1(x)$ is

$$\frac{(1-\epsilon)}{4}\left\{\int_0^{x_1}\phi_0(x)\frac{d^2}{dx^2}\mathrm{F}(x_1-x)dx+\int_{x_1}^{\infty}\phi_0(x)\frac{d^2}{dx^2}\mathrm{F}(x-x_1)dx\right\}.$$

Similarly, the second reflected distribution $\Phi_2(x)$ is

$$\frac{(1-\epsilon)}{4}\left\{\int_0^{x}\phi_1(x)\frac{d^2}{dx^2}\mathrm{F}(x_1-x)dx+\int_{x_1}^{\infty}\phi_1(x)\frac{d^2}{dx^2}\mathrm{F}(x-x_1)dx\right\},$$

etc., etc.

Adding the distributions

$$\begin{aligned}\phi_0(x_1)+\phi_1(x_1)+\phi_2(x_1)+\ldots\\ =\phi_0(x)+\frac{(1-\epsilon)}{4}\Bigg[\int_0^{x_1}\{\phi_0(x)+\phi_1(x)+\phi_2(x)+\ldots\}\\ \frac{d^2}{dx^2}\mathrm{F}(x_1-x)dx+\int_{x_1}^{\infty}\{\phi_0(x)+\phi_1(x)+\phi_2(x)+\ldots\}\\ \frac{d^2}{dx^2}\mathrm{F}(x-x_1)dx\Bigg].\end{aligned}$$

Now, writing the final distribution as $\Phi(x_1)$,

$$\begin{aligned}\Phi(x_1)=\epsilon\sigma\mathrm{T}^4+\frac{(1-\epsilon)}{4}\Bigg\{\int_0^{x_1}\Phi(x)\frac{d^2}{dx^2}\mathrm{F}(x_1-x)dx\\ +\int_{x_1}^{\infty}\Phi(x)\frac{d^2}{dx^2}\mathrm{F}(x-x_1)dx\Bigg\}.\end{aligned}$$

This equation could, of course, have been written down directly, as it merely expresses the fact that in the final steady state the total emission of radiation from any point is equal to the initial emission plus the reflected portion of the radiation received at that point from the whole of the cylinder.

The above equation is an integral equation of the second or Poisson's type. It does not appear to be possible to obtain an exact analytic solution for $\Phi(x)$, but an approximation which can attain whatever accuracy that is desired can be obtained by a method due to Whittaker *.

In Whittaker's paper it is shown, assuming certain existence theorems established by Volterra, that the solution of the integral equation

$$\phi(x)=f(x)-\int_0^x \phi(s)\kappa(x-s)\,ds,$$

where the nucleus $\kappa(x)$ is supposed to have been expressed approximately by Prony's † method as a series of exponentials of the form

$$\kappa(x)=B_1e^{\beta_1 x}+B_2e^{\beta_2 x}+B_3e^{\beta_3 x}+\ldots,$$

is
$$\phi(x)=f(x)-\int_0^x K(x-s)f(s)\,ds,$$

where
$$K(x)=C_1e^{\gamma_1 x}+C_2e^{\gamma_2 x}+C_3e^{\gamma_3 x}+\ldots,$$

in which there are as many exponential terms as there are in $\kappa(x)$.

In the case under consideration $f(x)$ is a constant (viz. $\epsilon\sigma T^4$), so that Whittaker's method suggests that the solution of the integral equation is of the form

$$\Phi(x)=(A_0+A_1e^{a_1 x}+A_2e^{a_2 x}+A_3e^{a_3 x}+\ldots)\sigma T^4.$$

This method has been used for the cases in which the nucleus $\dfrac{d^2}{dx^2}F(x)$ has been expressed as a single exponential and as the sum of two exponentials.

Now
$$\frac{d^2}{dx^2}F(x)=\frac{d^2}{dx^2}\left\{x^2+2-x\sqrt{x^2+4}\right\},$$

$$=2\left\{1-\frac{x(x^2+6)}{(x^2+4)^{3/2}}\right\}.$$

A set of values of $\dfrac{1}{2}\dfrac{d^2}{dx^2}F(x)$ is given in the table below for comparison with the corresponding values of e^{-x}, by which it may be seen that the function e^{-x} is a fair approximation to the function $\dfrac{1}{2}\dfrac{d^2}{dx^2}F(x)$.

A two-term exponential function $B_1e^{\beta_1 x}+B_2e^{\beta_2 x}$ giving an

* Whittaker, Proc. Roy. Soc. xciv. p. 367 (1918).

† Prony, *Journ. de l'École Pol.* Cah. ii. (an iv.), p. 29. See also Whittaker, *loc. cit.*, and Walsh, Proc. Phys. Soc. xxxii. pt. i. p. 26 (1919)

approximation to $\frac{1}{2}\frac{d^2}{dx^2}F(x)$ was obtained by determining the double exponential function, which had the same value as $\frac{1}{2}\frac{d^2}{dx^2}F(x)$ at four points including $x=0$ so that $B_1+B_2=1$, and then slightly adjusting β_1 and β_2 so that

$$\int_0^\infty (B_1e^{\beta_1 x}+B_2e^{\beta_2 x})dx=\frac{1}{2}\int_0^\infty \frac{d^2}{dx^2}F(x)dx=1;$$

i. e., making $$\left(\frac{B_1}{\beta_1}+\frac{B_2}{\beta_2}\right)=-1.$$

This adjustment makes the approximation to the radiation emitted from an annulus actually equal to the radiation emitted.

The third column in the table gives the values of $1{\cdot}21\,e^{-1{\cdot}14x}-0{\cdot}21\,e^{-3{\cdot}40x}$, which, as may be seen, gives a very close approximation to $\frac{1}{2}\frac{d^2}{dx^2}F(x)$ in the region where this function has any value of importance. Fig. 3 enables a graphical comparison of these functions to be made.

x.	e^{-x}.	$\frac{1}{2}\frac{d^2}{dx^2}F(x)$.	$1{\cdot}21\,e^{-1{\cdot}14x}-0{\cdot}21\,e^{-3{\cdot}40x}$.
0	1·0000	1·0000	1·0000
·10	·9048	·9252	·9302
·25	·7788	·8149	·8202
·50	·6065	·6433	·6459
·75	·4724	·4949	·4982
1·00	·3679	·3737	·3800
1·50	·2231	·2080	·2176
2·00	·1353	·1161	·1235
2·50	·0821	·0668	·0699
3·00	·0498	·0399	·0396
4·00	·0183	·0161	·0127

Assuming, then, that

$$\Phi(x)=(A_0+A_1e^{\alpha_1 x}+A_2e^{\alpha_2 x})\sigma T^4,$$

it is required to find A_0, A_1, A_2, α_1, and α_2 from the equation

$$\begin{aligned}A_0+A_1e^{\alpha_1 x_1}+A_2e^{\alpha_2 x_1}\\ =\epsilon+\frac{(1-\epsilon)}{2}\int_0^{x_1}&(A_0+A_1e^{\alpha_1 x}+A_2e^{\alpha_2 x})\\ &(B_1e^{\beta_1(x_1-x)}+B_2e^{\beta_2(x_1-x)})\,dx\\ +\frac{(1-\epsilon)}{2}\int_{x_1}^{\infty}&(A_0+A_1e^{\alpha_1 x}+A_2e^{\alpha_2 x})\\ &(B_1e^{\beta_1(x-x_1)}+B_2e^{\beta_2(x-x_1)})\,dx.\end{aligned}$$

Performing the integrations and equating the constant terms and the coefficients of $e^{\alpha_1 x_1}$, $e^{\alpha_2 x_1}$, $e^{\beta_1 x_1}$ and $e^{\beta_2 x_1}$ on each side of the equation, it is found that

$$\mathrm{A}_0=\epsilon-\mathrm{A}_0(1-\epsilon)\left(\frac{\mathrm{B}_1}{\beta_1}+\frac{\mathrm{B}_2}{\beta_2}\right)=\epsilon+\mathrm{A}_0(1-\epsilon),$$

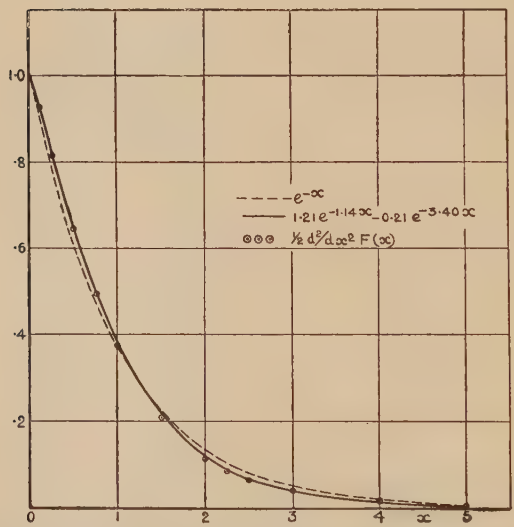
$$1=(1-\epsilon)\left\{\frac{\mathrm{B}_1\beta_1}{\alpha_1^2-\beta_1^2}+\frac{\mathrm{B}_2\beta_2}{\alpha_1^2-\beta_2^2}\right\},$$

$$1=(1-\epsilon)\left\{\frac{\mathrm{B}_1\beta_1}{\alpha_2^2-\beta_1^2}+\frac{\mathrm{B}_2\beta_2}{\alpha_2^2-\beta_2^2}\right\},$$

$$0=\frac{1}{\beta_1}-\frac{\mathrm{A}_1}{\alpha_1-\beta_1}-\frac{\mathrm{A}_2}{\alpha_2-\beta_1},$$

$$0=\frac{1}{\beta_2}-\frac{\mathrm{A}_1}{\alpha_1-\beta_2}-\frac{\mathrm{A}_2}{\alpha_2-\beta_2}.$$

Fig. 3.



Comparison of Single-term and Two-term Exponential Approximations with $\frac{1}{2}d^2/dx^2\,\mathrm{F}(x)$.

The first equation gives $\mathrm{A}_0=1$. The second and third equations show that α_1 and α_2 are given by the square roots of the roots of the quadratic equation in z:

$$(1-\epsilon)\left\{\frac{\mathrm{B}_1\beta_1}{z-\beta_1^2}+\frac{\mathrm{B}_2\beta_2}{z-\mathrm{B}_2^2}\right\}=1.$$

From the fourth and fifth equations the values of A_1 and A_2 can be obtained, using the values of α_1 and α_2 obtained from the second and third, while it can also be shown that $A_1+A_2=-(1-\sqrt{\epsilon})$.

The equations have been solved for the two exponential cases when $\epsilon=0{\cdot}75$, $0{\cdot}50$, $0{\cdot}25$, and $0{\cdot}10$ respectively, and the following expressions obtained, giving the distribution of radiation along the cylinders for these values of the emissivity :

$$\epsilon=0{\cdot}75,\quad (1-0{\cdot}1399\,e^{-0{\cdot}980x}+0{\cdot}0059\,e^{-3{\cdot}425x})\,\sigma T^4,$$

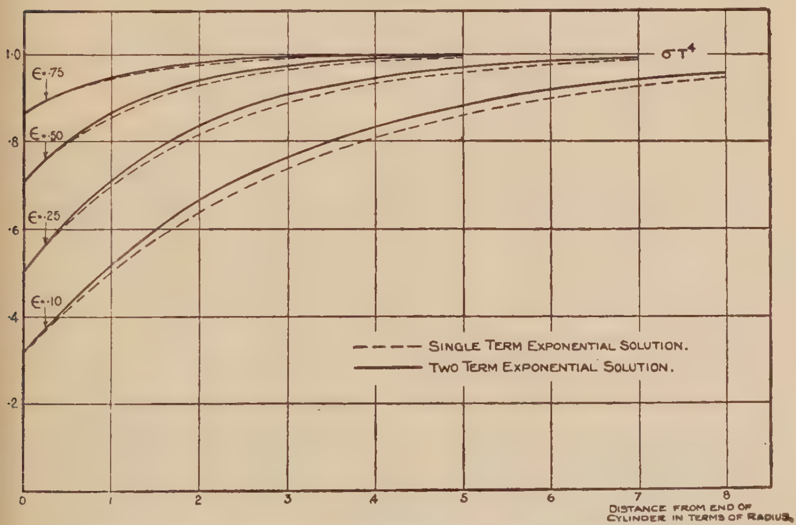
$$\epsilon=0{\cdot}50,\quad (1-0{\cdot}3013\,e^{-0{\cdot}795x}+0{\cdot}0090\,e^{-3{\cdot}450x})\,\sigma T^4,$$

$$\epsilon=0{\cdot}25,\quad (1-0{\cdot}5082\,e^{-0{\cdot}558x}+0{\cdot}0081\,e^{-3{\cdot}470x})\,\sigma T^4,$$

$$\epsilon=0{\cdot}10,\quad (1-0{\cdot}6893\,e^{-0{\cdot}352x}+0{\cdot}0057\,e^{-3{\cdot}485x})\,\sigma T^4.$$

These results are shown graphically by the full-line curves in fig. 4.

Fig. 4.



Distribution of Radiation near the end of a Uniformly-heated Infinite Cylinder.

The solution in the case of the single exponential case is obtained quite simply as $\{1-(1-\sqrt{\epsilon})\,e^{\sqrt{\epsilon}x}\}\,\sigma T^4$, and the results are also shown on fig. 4 by the dashed-line curves.

It will be noticed that for values of the emissivity greater than 0·50 the single-term exponential solution is very nearly the same as that of the two-term exponential. Considering

that the single exponential e^{-x} is only a moderately good approximation to $\frac{1}{2}\frac{d^2}{dx^2}\mathrm{F}(x)$, and that the results obtained by using it are close to the results obtained by using the quite good approximation given by the two-term exponential solution, it is probable that the slight improvement which could be obtained by using a three-term exponential approximation would not give appreciably different results from those shown by the full-line curves.

It will be noted that at the open end of the cylinder where $x=0$ the same result is obtained, using the single or the two-term experimental approximation to the function $\frac{1}{2}\frac{d^2}{dx^2}\mathrm{F}(x)$. This is quite general, and is in consequence of the approximations being adjusted to make

$$\int_0^{\infty} \Sigma\, \mathrm{B}e^{\beta x}\, dx = 1.$$

So that if $\frac{1}{2}\frac{d^2}{dx^2}\mathrm{F}(x)$ be expressed as $\Sigma_1^\infty \mathrm{B}_n e^{\beta_n x}$, then

$$\Sigma_1^\infty \mathrm{A}_n = -(1-\sqrt{\epsilon}),$$

and the value of $\Phi(x)$ at $x=0$ is

$$\mathrm{A}_0 + \Sigma_1^\infty \mathrm{A}_n = \sqrt{\epsilon}\sigma \mathrm{T}^4.$$

Since the approximation to $\frac{1}{2}\frac{d^2}{dx^2}\mathrm{F}(x)$ can be made as close as is liked, it follows that the value of $\Phi(x)$ at $x=0$ is exact.

Summary.

An expression is derived for the radiation from an annulus to any other annulus, and used to determine the radiation from any point inside an infinite circular cylinder of uniform temperature, multiple reflexion of radiation inside the cylinder being taken into account. The result is obtained in the form of an integral equation of the Poisson type, and an approximate solution is obtained. It is shown that the approximate solution is exact at the end of the cylinder, and that there the radiation emitted from the inside of the cylinder is given by $\sqrt{\epsilon}\sigma \mathrm{T}^4$ per unit area, where ϵ is the emissivity of the walls of the cylinder.

The author wishes to express his thanks to Mr. R. A. Frazer for the interest he has taken in this problem and the benefit he has received by discussing it with him.

LXVIII. *Multiple Ionization in X-Ray Levels.* *By* Prof. H. R. ROBINSON, *University College of South Wales and Monmouthshire* *.

§ 1. THE terms of the X-ray spectra of the elements ("spectra of the first kind") are now very accurately known in the majority of cases. It is some years since the first comprehensive tables of term values were published by (*inter alia*) Sommerfeld and Bohr & Coster. These tables were based largely on emission spectra measured in Siegbahn's laboratory, together with a judicious selection of combinations with known absorption limits. More recent work has, in the main, confirmed the remarkable accuracy of these early tables, though the natural development of spectroscopic research has enabled minor corrections and additions to be made in some instances. Work still remains to be done on the terms of lower frequency, but in the normal X-ray regions the existing data may be regarded as sufficiently complete; the most urgent need is not for increased accuracy in the normal term values, but rather for some detailed knowledge of the terms in atoms which are ionized to different degrees in their X-ray levels.

§2. The energies associated with atoms of the latter class are, according to the theory first elaborated by Wentzel †, intimately related to the frequencies of the "non-diagram" lines in X-ray spectra—*i. e.*, those faint lines which cannot be fitted into the accepted scheme of X-ray levels, even by allowing violations of the selection rules. These lines (usually satellites on the high-frequency sides of the normal series lines) are supposed to originate in transitions between states of multiply-ionized atoms; for this reason Wentzel has called them X-ray "spark" lines, although the normal X-ray lines are, in the optical sense, spark lines. Wentzel speaks of spark lines of the first, second, ... order according as the atom is doubly, triply, ... ionized—corresponding to the "spectra of the second, third, ... kind" of Bohr and Coster's notation.

In its broad outlines Wentzel's theory has provided an eminently satisfactory explanation of the origin of spark lines. Support has been brought to the theory by a number of investigations of the conditions necessary for the appearance of the satellites. Coster ‡ first showed, in the course

* Communicated by the Author.

† Wentzel, *Annalen der Physik*, lxvi. p. 437 (1921); lxxiii. p. 647 (1924).

‡ Coster, Phil. Mag. xliii. p. 1070, xliv. p. 546 (1922).

of a very detailed investigation of X-ray spectra, that the satellites in the L spectrum of silver were practically suppressed if the voltage on the X-ray tube was kept sufficiently low (say about 1 kilovolt above the critical L excitation potentials). Much other indirect evidence of this kind has since been obtained, all indicating that the appearance of the satellites is favoured by the use of vigorous excitation.

§ 3. It cannot, however, be said that there is anything like a complete confirmation of the details of the original scheme propounded by Wentzel. According to this scheme, the K spark lines correspond to the following transitions :—

$$K\alpha_3 = KL \rightarrow L^2, \quad K\alpha_4 = K^2 \rightarrow KL, \quad \text{(First order)},$$
$$K\alpha_5 = KL^2 \rightarrow L^3, \quad K\alpha_6 = K^2L \rightarrow KL^2 \quad \text{(Second order)},$$
$$K\alpha' = KM \rightarrow LM,$$

the symbol K^2L being used to represent an atom which has lost both K electrons and one L electron, and so on. It will be noticed that no attempt is made to discriminate between the various L and M sub-levels ; in any case, as was first shown by Wentzel * in a later paper, there is reason to believe that the multiplicity of these levels is profoundly modified by the multiple ionization of the atom.

Fairly full complements of K spark lines have been measured for only a few of the lighter elements, and the observational data are too meagre to permit of a thorough numerical comparison between experiment and theory. The evidence in favour of the scheme is restricted to the observation, over a very limited range, of certain regularities, predicted by the theory, in the frequency differences $\alpha_6-\alpha_4$, $\alpha_5-\alpha_3$, $\alpha_3-\alpha_1$, for a given element, and the approximate equality of $\alpha_6-\alpha_4$ for each element with $\alpha_3-\alpha_1$ for the element of next higher atomic number.

In the case of the spark lines associated with the L series, Wentzel has suggested for the most prominent satellites, $L\alpha_3$ and $L\alpha_4$, the transitions

$$L\alpha_3 = LM \rightarrow M^2,$$
$$L\alpha_4 = L^2 \rightarrow LM.$$

Here, of course, and also in the M series, there is a great variety of levels to select from, and it is difficult to decide, on the available experimental evidence, in favour of any particular scheme of transitions. One great difficulty lies in the nature of the measurements ; the spark lines cannot, as

* Wentzel, *Zeits. f. Phys.* xxxi. p. 445 (1925).

a rule, be measured with the same accuracy as the normal series lines. The latter are always heavily over-exposed relatively to the former, and this, naturally, does not make for the accurate measurement of close satellites. It is therefore unlikely that we shall have for some time any appreciably more precise knowledge of the frequencies of the spark lines, or any extension to measurements for the heavier elements, where the separations are still less and the spark lines less prominent.

§ 4 The indirect evidence is also, from the point of view of the scheme, far from satisfactory. There is, in fact, no clear-cut indication of the exact stages of ionization involved in the production of spark lines, or of the manner in which the ionization is brought about. Wentzel's original assumption (abandoned later) of a process of cumulative ionization by successive electron impacts on the same atom seems to be definitely put out of court by the theoretical considerations advanced by Rosseland*. The experimental evidence is also against this theory—all tests, so far, indicate high voltage on the X-ray tube, rather than heavy milliamperage, as the deciding factor in the production of spark lines. Coster's experiments, referred to above, were not carried out under sufficiently definite conditions to furnish a precise estimate of the minimum excitation potential for spark lines. Later experiments have, in a few instances, fixed the critical potentials within narrower limits: the results indicate that, on the theory of multiple ionization by a single electronic impact, Wentzel's scheme requires modification in some of its details. At the same time the results are neither sufficiently numerous nor sufficiently precise to define any more acceptable scheme.

Bäcklin †, investigating the K spectrum of aluminium with different exciting voltages, found that $K\alpha_4$ appeared at a voltage well below the calculated minimum value required for double ionization of the K level. Further, allowing for possible errors in estimating the voltages, it seemed probable that $K\alpha_6$ also appeared below this critical value. The feeble intensity of the spark lines makes the exact measurement of the corresponding critical potentials very difficult; this factor might lead to an over-estimate of the values, but it leaves no loophole for spark lines which appear at unduly low voltages. Another important point brought out by Bäcklin's work was that the ratio of the intensities of $K\alpha_3$

* Rosseland, Phil. Mag. xlv. p. 65 (1923).
† Bäcklin, *Zeits. f. Phys.* xxvii. p. 30 (1924).

and $K\alpha_4$ was sensibly independent of the exciting voltage. This would only fit in with Wentzel's original scheme if it could be assumed that simultaneous KL ionization by a single electron occurred much less frequently than simultaneous K^2 ionization (the end state for $K\alpha_4$ being identical with the initial state for $K\alpha_3$). The evidence of Bäcklin's work is therefore strongly against any scheme which requires K^2 states for the explanation of the K spark lines *.

It may be mentioned here that in a recent paper (received after the greater part of the present paper had been written) Saha and Ray † have, on purely theoretical grounds, propounded a scheme for the spark lines which does not involve K^2 states.

Siegbahn and Larsson's ‡ observations on the $L\alpha$ satellites of molybdenum are of special interest, and are probably the most accurate available. The critical L_I, L_{II}, L_{III} excitation voltages for molybdenum are approximately 2880, 2620, and 2520 respectively. For normal K excitation the minimum is 19,950 volts. Siegbahn and Larsson find four satellites on the high-frequency side of $L\alpha_{1,2}$ at all voltages above 4000. No new satellites appear between 4000 and 20,000 volts, but a fifth (with possibly, but very doubtfully, a sixth) faint satellite of still higher frequency appears at and above 20,000 volts. No further satellites appear in this region, even at 40,000 volts—the highest potential used.

The satellites lie within the shadow of the intense $L\alpha_1$ line, but the evidence of the photometric analyses of the spectrograms is extraordinarily clear and convincing. The spark lines may be picked out with ease, and some estimate may be obtained of their relative intensities. The following points of primary importance emerge from the study of the spectrograms:—

(1) The intensities of the satellites, relative to that of $L\alpha_1$, are practically unchanged between 4 and 15 kilovolts, and probably up to 20 kilovolts, though no curves are given for the range 15–20 kilovolts.

(2) Not only does a new satellite (or two new satellites) appear, as mentioned above, at 20,000 volts—*the K excitation limit*—but the intensities of all the satellites, relative to that of $L\alpha_1$, increase very appreciably at this stage. Siegbahn

* See, however, Wentzel, *Zeits. f. Phys.* xxxi. p. 450 (1925).

† Saha & Ray, *Phys. Zeitschr.* xxviii. p. 221 (1927).

‡ Siegbahn & Larsson, *Ark. f. Mat. Ast. och Fys.* xviii. no. 18 (1924). Some of the curves are reproduced in Lindh's Report (*Phys. Zeits.* xxviii. p. 93, 1927).

and Larsson have not mentioned this latter point in their discussion. They state at one point that their curves do not correctly represent the relative intensities of the lines, and this contention is certainly justifiable, as $L\alpha_1$ is heavily over-exposed. It seems, however, fair to assume that the marked sudden increase in the strength of the satellites at 20,000 volts is a real effect. Taking the curves as they stand, the relative intensities of the satellites between 20 and 40 kilovolts are at least two and a half times greater than they are below 20 kilovolts. If anything, the satellites appear relatively a little feebler at 40 than at 20 kilovolts; but there is little justification (and no sufficiently attractive pretext) for straining the interpretation of the curves so far as to insist upon this point. It may, then, be taken from the curves that no new satellites, and no marked discontinuities in the intensities of the existing satellites, appear between 20 and 40 kilovolts.

Taking these points in turn:—

(1) It is hardly conceivable that a 4000-volt electron is capable of removing two L electrons from a molybdenum atom. It therefore seems likely that, at all events, the stronger L satellites do not originate in transitions from L^2 states. This is closely analogous with Bäcklin's results for the K spark lines.

(2) I have already referred, in a recent letter to 'Nature' *, to the fact that a rapid increase in the rate of production of atoms in L^2, LM, ... states is to be expected after the K critical excitation potential is over-stepped. After the removal of a K electron from an atom, there frequently ensues either (*a*) the genesis, immediately followed by specially privileged "internal absorption," of a K series X-ray, or (*b*) a "radiationless" reorganisation of the extra-nuclear electrons, accompanied by the expulsion of a "photo-electron of the second kind," generally from one of the X-ray levels. For the present purpose the exact nature of the process is immaterial, though it is noteworthy that Ellis † (to whom we owe most of our knowledge of the details of the internal conversion of γ rays) leans to the view that his experiments deal with a true internal absorption of radiation. The experimental evidence is less definite in the case of X-rays, where, as Ellis has pointed out, the conditions are not identical with those of his experiments.

* Robinson, 'Nature,' cxviii. p. 224 (1926).

† See, in particular, Ellis & Wooster, Roy. Soc. Proc. A, cxiv. p. 285 (1927).

The point has been discussed in some detail by Smekal *, among others.

So far as the present discussion is concerned, the important point is that, whatever the exact nature of the process by which the potential energy of the excited atom is internally converted, the final result of the process is an atom which is multiply ionized in its X-ray levels. Some of the direct experimental evidence for this will be found summarized in the above-mentioned letter to 'Nature,' and more fully in a recent paper in the 'Proceedings of the Royal Society' †. The effectiveness of this mode of production of multiply-ionized atoms is strongly indicated by the evidence in (2) above, and more particularly by the marked increase in the intensities of the $L\alpha$ satellites above the K excitation limit.

This forms a striking parallel with the fact, predicted by the original Kossel scheme of X-ray spectral series, that the inception of K emission must always be accompanied by a corresponding increase in the L emission. This effect has recently been verified by Stumpen ‡, whose isochromatic curves for the lines of the L series all show distinct upward inflexions of the K excitation voltage.

If any appreciable KL ionization occurred under the conditions of Siegbahn and Larsson's experiments, it would be expected to manifest itself, possibly by the appearance of new L spark lines, and certainly by an increase in the relative intensities of the existing spark lines. The absence of these effects between 20 and 23 kilovolts—and even up to, and presumably beyond §, 40 kilovolts—strongly suggests that ionization of the K level and an L level by the same cathode ray is relatively infrequent—that is, compared with the frequency of the occurrence of L^2, LM, ... ionization by "internal absorption of fluorescent X radiation." ‖

§ 5. In the meantime a very important contribution to the problem of the spark lines has been made by Coster and Druyvesteyn ¶. It had previously been suggested (originally, I believe, by Coster himself) that the spark

* Smekal, *Ann. der Phys.* lxxxi. p. 391 (1926) ; *Phys. Zeitschr.* xxvii. p. 831 (1926).

† Robinson & Cassie, Roy. Soc. Proc. A, cxiii. p. 282 (1926).

‡ Stumpen, *Zeits. f. Phys.* xxxvi. p. 1 (1926).

§ In Siegbahn & Larsson's work a transformer was used to excite the X-ray tube at the highest voltages, and it seems very likely that the peak voltage may have been high enough for K^2 excitation.

‖ The process will be so described for the sake of brevity.

¶ Coster & Druyvesteyn, *Zeits. f. Phys.* xl. p. 765 (1927).

lines would probably be absent from fluorescently excited X-ray spectra; this supposition was apparently confirmed experimentally by Dauvillier *. Coster and Druyvesteyn have now, however, succeeded in exciting K spark lines by fluorescence, using an X-ray tube specially designed to produce intense fluorescent X-radiation in a secondary radiator. Photographs of the K spark lines of iron have been obtained from an iron radiator, placed 5 mm. away from the copper anticathode of the primary tube, with exposures of approximately 400 milliampere-hours at 30 kilovolts. Some idea of the efficiency of the process is given by the authors' statements that under the same conditions the normal $K\alpha$ doublet was well exposed with 8 milliampere-hours, while the direct radiation from the same tube, fitted with an iron anticathode, gave the Fe $K\alpha$ doublet with about $\frac{1}{4}$ milliampere-hour.

Three possible modes of production of doubly-ionized states by the action of X-rays are briefly discussed by Coster and Druyvesteyn. In view of the importance of the problem, these discussions are reproduced, and to some extent amplified, below.

(1) The most direct of all possible processes—the absorption of a quantum of X-radiation, resulting in the simultaneous ejection of two electrons from X-ray levels—is difficult to support by direct experimental evidence. Siegbahn is reported to have observed, in the case of sulphur, a faint absorption discontinuity, corresponding approximately to the frequency required for the simultaneous removal of the two K electrons. So far as I am aware, no detailed confirmation of this report has yet appeared. The discontinuity in question must be extremely faint, or it could hardly have escaped the observation of previous workers on absorption limits. Coster and van der Tuuk † have sought in vain for corresponding effects in argon; Coster and Druyvesteyn, however, point out that effects much larger than that required to account for the observed intensities of the spark lines could very well have escaped detection in the absorption experiments. The maximum intensity of the impulse radiation in the primary beam used to excite the spark lines (copper anticathode, 30 kilovolts) would lie in the region of frequencies corresponding to a little over 20 kilovolts: there would therefore be present very intense radiations of sufficiently high frequencies to produce KL and K^2 states in

* Dauvillier, *C. R.* clxxvii. p. 167 (1923).

† Coster & van der Tuuk, *Zeits. f. Phys.* xxxvii. p. 367 (1926).

single absorption processes. Processes of this kind do not appeal as very likely ones, but the evidence so far available does not rule them completely out.

(2) Double ionization of an atom by a high-speed photo-electron from a neighbouring atom. Quite apart from other and obvious objections to this view, Coster and Druyvesteyn show clearly that the observed intensities of the spark lines are far too high to be accounted for in this way.

(3) A photo-electron expelled with sufficiently high speed from (say) the K level may, on its way out, eject another electron from an X-ray level of the same atom. K^2, KL, . . . states can clearly arise in this way, given a primary X radiation of sufficiently high frequency. A somewhat similar succession of events may readily be visualized in the case of double ionization by a high-speed electron. Coster and Druyvesteyn show that the relative intensities of the spark and normal lines, produced by bombardment of an anticathode with cathode rays of suitable speed, are in rough agreement with the relative numbers of KL and K states predicted by Rosseland's* extension of Sir J. J. Thomson's† theory of ionization by charged particles.

If this view, favoured by Coster and Druyvesteyn, of the processes leading to double ionization is accepted—and it has obvious attractions,—the evidence is again opposed to the attribution of the K spark lines to transitions from K^2 states. The number of such states predicted by the theory is far too small to give the observed intensities of the spark lines. It should, however, be mentioned that this argument tacitly assumes that the proportions of radiationless rearrangements are not vastly different for K and KL states.

Further, a very simple consideration (viz. of the differences between the processes of single ionization by X- and cathode-rays) indicates that, on this view, for a given intensity of the normal K spectrum, the spark lines in the spectrum excited by electronic bombardment should have, very roughly, double the intensities of the same lines in the "fluorescent" spectrum. An intensity difference of this order is, in fact, exhibited by the photometric curves of Coster and Druyvesteyn (*loc. cit.* p. 779), though the comparison is necessarily very rough.

§ 6. The question of the exact mode of generation of doubly-ionized atoms is of the first importance in connexion with projected measurements of the energies associated with

* Rosseland, *loc. cit.*

† Thomson, Phil. Mag. xxiii. p. 449 (1912).

the corresponding states. It seems sufficiently clear that only the first mode contemplated in § 5—double ionization in a single absorption act—will give a sharply-defined limiting frequency. If Siegbahn's observation of absorption edges for K^2 states can be confirmed and extended to KL, ... states, the measurement of these edges may be expected to provide the most accurate determinations of the energies. At present, however, the experimental evidence strongly suggests that double ionization processes of this kind, if indeed they occur at all, do not occur sufficiently often to give well-marked absorption edges under ordinary experimental conditions.

If the process of double ionization occurs in accordance with the scheme of alternative (3) above, as seems highly probable—*i. e.*, in two steps—it will clearly be very difficult to fix the energies with any great accuracy by direct experiment. The details from Coster and Druyvesteyn's paper, quoted in § 5 above, are a sufficient indication of the faintness of the spark lines. Further experiments are promised in which an attempt is to be made to trace the effect upon the spark lines of varying the frequency of the primary beam. The results of these experiments will be awaited with the deepest interest, as a step towards the solution of the problem of the origin of the spark lines. It is, however, obvious from the outset that there are sufficiently formidable experimental difficulties to prevent any accurate determination of critical excitation frequencies for the spark lines. Abrupt variations in the intensities of the spark lines at the critical frequencies are not to be expected, and the photographic method is probably the only one which can be used for detection of lines so feeble as those under investigation. Similar objections would apply to attempts to refine upon the methods of Bäcklin's experiments; it would hardly appear feasible, with the intensities available, to utilize the ionization spectrometer to obtain the isochromatic curves for even the strongest of the spark lines. It would appear that the most that can be hoped from these experiments is a sufficiently close approximation to the critical energies to place beyond doubt the degree and type of ionization in the initial state.

§ 7. The method of measuring the energies of the tertiary photo-electrons ("photo-electrons of the second kind"), which has already been applied to a limited extent in the work of Robinson and Cassie, in many respects offers unique advantages. The chief difficulty lies in the interpretation

of the lines of the corpuscular "spectra," and the method has one other inherent defect: obviously, the only "radiation" available for the expulsion of an electron from the L level of an ionized atom is the K-radiation from the same atom, and so on. The frequencies of the K-radiations are always large in comparison with the critical L excitation frequencies; the disproportion is less marked in the case of the L lines and the M limits, but even here it is sufficient to impair the "resolving power" of the apparatus. For this reason it is not possible to use the method of corpuscular spectrometry quite so effectively in these cases as for the secondary electrons which result from the external absorption of a selected primary radiation. On the other hand, the lines obtained are extremely sharp, and may be measured with very high precision; further, by suitable selection of the source of X-rays, it is always possible to check the measurements by bringing some standard line (corresponding to secondary electrons ejected from a normal level of the target material by a characteristic radiation in the primary beam) into the region of the photographic plate in which the measurements are being made. Most important of all, the process of internal absorption is so remarkably efficient that measurable photographs may be obtained with relatively short exposures, and the definition of the lines is not impared by the overlapping of lines due to "photo-electrons of the first kind"*. This is in accordance with the evidence deduced from Siegbahn and Larsson's work (§ 4, p. 766), to the effect that internal absorption of X-radiation is by far the most efficient mode of production of multiply-ionized atoms.

The "fluorescent" lines already measured (Robinson and Cassie, *loc. cit.* pp. 284 *et seqq.*) are sufficient to show the possibilities of the method of corpuscular spectrometry, although the measurement of these lines was in this instance subsidiary to another investigation, and no attempt was made to exhaust the series of fluorescent lines for any element. The order of accuracy attained is indicated by the marked differences recorded (for instance) for the energies of the L levels of the ionized copper atom, according to whether the electron is ejected therefrom by internal absorption of $K\alpha_1$ ($L_{III} \rightarrow K$) or $K\beta_1$ ($M_{III} \rightarrow K$).

These experiments were interrupted by the departure of Mr. Cassie and myself from Edinburgh last year.

* *I. e.*, electrons ejected by the fluorescent X-radiation of one atom from the X-ray levels of a neighbouring (originally neutral) atom.

I am now continuing the experimental work with Mr. C. L. Young; we hope, in spite of temporary disturbances occasioned by the necessity for partially gutting and refitting the laboratory, to be able shortly to communicate an extended list of the energy levels of doubly-ionized atoms. It is noteworthy that in the case of internal absorption of K characteristic radiations, the strongest lines so far measured apparently correspond to LM states of the atom concerned, although L^2 states would at first sight appear to be a probable result of the internal absorption of $K\alpha(L \rightarrow K)$. The results of our experiments are thus in excellent accord with the deductions from Siegbahn and Larsson (§ 4, p. 766), that the principal L spark lines originate in transitions from LM and lower states, and not from L^2 states of the atom. The point of particular importance in this connexion is that Siegbahn and Larsson's curves show a marked increase in the intensity, rather than in the type, of the spark spectrum exactly at the point where our experiments indicate an increased production of LM (and LN) states. The new faint satellite(s) found by Siegbahn and Larsson at and above 20,000 volts might conceivably be due to L^2 states produced by internal absorption.

Similarly, the fluorescent corpuscular lines arising from the internal absorption of the L-radiations appear generally to come from atoms which are left in MN, ... states, though here the interpretation is more ambiguous. The interpretation would in all cases be greatly simplified if it were certain that we had to deal with a true internal absorption of characteristic radiations, in which case valuable guidance could be derived from the known intensity ratios and selection rules, and from the approximately known variations in the intensities of the corpuscular spectra with the frequency of the exciting radiation. It is, unfortunately, quite clear that there are fundamental differences between "internal" and "external" absorption (Robinson, 'Nature,' *loc. cit.*), and much work is still required on the theoretical side of the problem of the radiationless changes. There is also the additional complication of the increased multiplicity of the terms in the ionized atoms (Wentzel, reference in § 3, p. 764). It is evident that a great deal of information is still to be derived from the closer study of the fluorescent lines of the corpuscular spectra—both of the absolute energies of the lines and of their relative intensities,—though it seems probable that the resolving power will have to be increased if the method is to be utilized to the fullest advantage.

Note added in proof.—Reference may be made to two very recent papers which appeared in the *Zeitschrift für Physik* during July 1927. (1) Wentzel has calculated, on wave-mechanical theory, the relative probabilities of different internal rearrangements in an atom initially ionized in the K level; the results of the calculation are in general agreement with the intensities recorded by Robinson and Cassie. (2) Druyvesteyn has communicated the results of new and extensive measurements on spark lines in the K and L series of a number of elements. This work appears to constitute a distinct advance towards the establishment of a satisfactory scheme for the spark lines.

LXIX. *On the Arc Spectrum of Bismuth.* *By* G. R. Toshniwal, *M.Sc., Research Scholar, Allahabad University, Allahabad* *.

SUMMARY.

The arc spectrum of Bismuth has been investigated in the heavy arc and under-water spark, and the lines remeasured between λ 1900 and λ 3550. A discussion of the structure of the spectrum of Bismuth from the standpoint of the theories of complicated spectra is given. It is shown that in Bismuth, owing to its large atomic number, terms arising from the same level are separated by widely different values, and this renders the interpretation of the spectrum rather difficult. A large number of new lines has been obtained and a number of important lines has been carefully remeasured. The new lines include some predicted by Thorsen.

The arc spectrum of Bismuth is interesting from more than one point of view. Thirty years ago Kayser † and Runge tried to discover regularities, and found that the spectrum consisted of groups of lines having the separations 11418, 4019, and 6223. The last group consisted in some cases of close doublets with the separation 1·91. Ruark, Mohler, Foote, and Chenault ‡ investigated the excitation and the ionization potential of the element by the electron bombardment method. They arranged the lines in a number of fundamental levels (denoted by $3d_2$, $3d_1{}^B$, $3d_1{}^A$, ... etc.) and sub-levels (denoted by Greek letters α, β, γ, δ, ... etc.).

* Communicated by Prof. M. N. Saha, D.Sc., F.R.S.

† Kayser, *Handbuch der Spectroscopie*, ii. p. 576.

‡ Ruark, Mohler, Foote, and Chenault, Sc. Pap. Bur. Stand. xix. p. 463 (1923–24).

They added with some hesitation two levels, $1s$ and β, to those given by Kayser and Runge. While this paper was being written there appeared a paper by Thorsen (*Zeitschrift für Physik*, xl.), who tried to discover Rydberg sequences in the spectrum of Bismuth.

On the experimental side, Offermann * gave an accurate measurement of wave-lengths from λ 6134 to λ 2061. Randall † has explored the infra-red region from λ 9600 to λ 22000 by means of a grating, a thermopile, and a Paschen galvanometer. Walters ‡ has measured the wave-lengths in the arc spectrum within the region λ 5600 to λ 9600 by means of infra-red photography. Takamine and Nitta have measured the spectrum on the short wave-length side of λ 1990, and Bloch § and McLennan ‖ in the Schumann region down to λ 1400. The Zeeman effect has been studied by Purvis ¶, but the data do not seem to be reliable.

The spectrum of Bismuth has been investigated several times in this laboratory by Dr. N. K. Sur in the furnace and the under-water spark. The results were not published in the expectation of a more extensive investigation. I took up the work started by Dr. Sur and have investigated the spectrum of the 20–21 ampere arc.

The region λ 4800 to λ 3550 was photographed by means of a 5-ft. Rowland grating (dispersion 11·12 Å. to a mm.); from λ 3550 to λ 2170 was investigated on quartz spectrograph E. I. (Adam Hilger), kindly lent to us by Prof. N. R. Dhar, of the Chemistry Department; and from λ 2170 to λ 1900 on the above-mentioned grating and also on a small quartz spectrograph E. 126. Comparison spectra of iron were taken up to λ 2300, that of the copper arc from λ 2300 to λ 2170, and that of the silver spark down to λ 1900.

My measurements substantially agree with those of Offermann; the differences between the two greater than ·02 Å. have been noted down. Offermann's data are used between λ 3500–λ 4800, since my measurements of the plates in this region cannot be accurate in the second decimal place, because of the small dispersion in the first order of the grating. The lines marked by T in this region are new lines, and there is a possible mistake of not more than ·08 Å.

* Offermann, Kayser, and Könen, *Handbuch der Spectroscopie*, vol. vi. p. 104.

† Randall, Astro. Journ. xxxiv. p. 1 (1911).

‡ Walters, Sc. Pap. Bur. Stand. p. 411 (1921).

§ L. and E. Bloch, *C. R.* clxx. p. 320; clxxi. p. 709 (1920).

‖ McLennan, Young, and Ireton, Proc. Roy. Soc. xcviii. p. 95 (1920).

¶ Purvis, Proc. Camb. Phil. Soc. xiv. p. 216 (1907).

Between λ 2170 and λ 1900 my measurements differ considerably from those by Eder and Valenta, and recorded by the Bureau of Standards' investigators already mentioned. The order of mistake in this region is not more than ·08 Å.U.

Besides the lines already recorded in this region, I have discovered a large number of new lines which have been denoted by the letter T. I have looked for the impurity lines of Si, Pb, Ag, Tl, C, Bi, As, Sb, Sn, Zn, etc., and also for air-lines with the aid of the tables given in vols. vi. and vii. of Kayser's 'Handbuch der Spectroskopie.'

Table I. gives a list of the Bismuth arc lines with wave-numbers and classification.

Table I.

λ_{air} I. A.	Int.	$\nu_{vac.}$	Classification.	Remarks.
1902·16	1	52612		
1909·6	2 R	52352	......	Observed by Sur in absorption.
1913·75	3	52236·3		
1930·42	3 R	51785·0	......	T.
1953·89	8 R	51163·2	$^4S_2-J_3$	
1959·48	8 R	51017·3	$^4S_2-I_2$	Bloch (1959·63).
1973·08	5	50665·7	$^2D_3-C_2$	Bloch, 1973·15.
1976·42	1	50580·1	......	T.
1984·5	2 U	50374·0	......	T.
1989·96	5	50235·8		
2001·59	2 U	49944·0	......	T.
2011·39	1 *u*	49700·7	......	T.
2021·21	6 R	49459·3	$^4S_2-H_2$	Eder, 2020·51 in vac.
2023·99	5 *u*	49391·3	......	T.
2033·91	1 U	49150·5	......	T.
2041·96	8	48956·8	......	T.
2049·69	7 R	48772·1	......	Eder, 2049·59 in vac.
2053·52	1 *u*	48681·2	......	T.
2057·68	5	48582·8	$^2D_3-b_2$	T.
2061·70	10 R	48488·1	$^4S_2-G_3$	Offermann, 2061·73.
2064·79	5	48415·5	......	T.
2069·70	1	48300·7	......	T.
2097·63	1 U	47657·6	......	T.
2110·31	10 R	47371·3	$^4S_2-F_1$	Offermann, 2110·26.
2133·69	6 R	46852·3	$^2D_2-N_2$	Offermann, 2133·62.
2134·58	6 R	46832·8	......	Offermann, 2134·31.
2143·66	1	46634·4	......	T.
2152·91	6 R	46434·0	......	Offermann.
2153·53	6 R	46420·7	......	Offermann.
2156·96	7 R	46347·0		

TABLE I. (*continued*).

λ_{air} I. A.	Int.	$\nu_{vac.}$	Classification.	Remarks.
2164·10	4 R	46194·1	......	Offermann.
2176·62	0 R	45928·4	......	Ruark etc. give its intensity as 6 R. But a very faint trace of this line appears on only one plate.
2177·22	4 R	45915·7	$^4S_2-E_1$	Ruark etc., 2177·33.
2189·58	8 R	45656·6	$^2D_2-M_3$	
2198·26	1 R	45476·3	......	T.
2202·86	2 RU	45381·3	......	T.
2203·12	4 u	45376·0	......	Offermann. Not present on my [plates.
2214·11	3 R	45150·7	$^2D_2-L_2$	
2224·24	2	44945·1	......	Offermann, 2224·21.
2228·23	10 R	44864·6	$^4S_2-D_2$	
2230·64	10 Ru	44816·4	$^4S_2-C_3$	
2237·84	1 R	44672·0	......	T. [Tl.?].
2246·77	1 u	44494·5	......	T.
2249·38	5	44442·9	$^2\overline{P}_1-c_2$	T.
2276·57	10 R	43912·2	$^4S_2-B_2$	
2281·38	6 u	43819·5	......	Offermann (2281·35).
2288·00	1	43692·8	......	T.
2289·98	1	43655·0	......	T.
2293·87	1 u	43582·0	......	T. ?
2297·58	1 v	43510·6	......	T.
2304·94	1 v	43371·7	......	T.
2309·73	3 U	43381·7	......	Offermann, 2309·3.
2313·80	1 R	43205·6	$^4S_2-a_3$	T.
2316·1	1 U	43162·7	......	T.
2317·43	1 r	43138·0	......	T.
2328·19	7 r	42938·6	......	Offermann, 2328·24.
2329·95	1	42906·2	......	T.
2333·79	7	42835·6	$^2D_3-N_2$	
2337·49	1	42767·8	......	T.
2345·91	5 u	42614·3	......	T.
2347·89	0 U	42576·4	......	T. ?
2349·10	3	42556·5	$^2D_2-k_2$	T.
2353·61	1	42474·9		
2354·60	4 u	42457·0	......	O., 2354·48.
2360·09	1 U	42358·1	$^2\overline{P}_1-b_2$	T.
2368·18	1 r	42213·6	......	T.
2369·21	6 u	42195·2	......	O., 2369·17.
2379·73	5 u	42008·7	......	T.
2400·90	10 R	41638·4	$^2D_3-M_3$	
2409·57	2 U	41488·5	......	O., 2409·62.
2430·45	3 u	41132·1	$^2D_3-L_2$	
2433·4	3 U	41082·3	......	? O.
2435·81	2 U	41041·8	......	T.
2448·30	8 r	40832·3	$^2D_2-d_2$	O., 2448·06.
2489·6	3 U	40155·0	......	O., 2489·4.

TABLE I. (*continued*).

λ_{air} I. A.	Int.	$\nu_{vac.}$	Classification.	Remarks.
2499·52	10	39995·6	......	O., 2499·30.
2515·68	9 R	39738·7	$^2D_2-J_3$	
2524·53	9 R	39599·5	$^2D_2-I_2$	
2532·2	5 U	39479·5	......	O., 2532·5.
2536·56	1 R	39411·63	......	T. ?, Hg.
2582·20	4	38715·1	......	O., 2582·15.
2594·12	1	38537·2	$^2D_3-k_2$	O., 2594·03. My measurement is uncertain, as the line was not visible under microscope.
2600·61	0	38441·04	......	O. ?
2627·92	8 R	38041·6	$^2D_2-H_2$	
2696·76	6 R	37070·5	$^2D_2-G_3$	
2730·45	6 *u*	36613·2	$^2\overline{P}_1-N_2$	O., 2730·51.
2767·88	3	36118·1	......	T.
2780·52	8 R	35953·9	$^2D_2-F_1$	
2798·74	6 *u*	35719·8	$^2D_3-J_3$	O., 2798·70.
2803·53	4	35658·8	......	T. (Bi+) ?.
2809·64	6 R	35581·4	$^2D_3-I_3$	
2864·01	7 U	34905·8	$^2\overline{P}_1-L_2$	O., 2863·75. My measurement
2883·81	1 *u*	34666·2	......	O. ? [uncertain; line very diffuse.
2892·91	1 *u*	34557·1	......	O. ?
2897·99	9 R	34496·6	$^2D_2-E_1$	
2938·32	9 R	34023·1	$^2D_3-H_2$	
2944·28	0	33954·3	......	O. ?
2989·05	7 R	33445·8	$^2D_2-D_2$	
2993·36	6 R	33397·5	$^2D_2-C_3$	
3024·67	7 R	33052·0	$^2D_3-G_3$	
3035·18	7 *u*	32937·5	$^2\overline{P}_2-c_2$	O., 3034·91.
3067·73	10 R	32587·9	$^4S_2-{}^4P_1$	
3076·69	2 R	32493·0	$^2D_2-B_2$	
3093·58	5 *u*	32315·7	$^2\overline{P}_1-k_2$	T.
3144·6	5 U	31791·4	$^2D_2--a$	T.
3216·8	1 U	31077·8	......	T.
3239·73	5	30887·9	$^2\overline{P}_2-b_2$	T.
3267·97	1 *u*	30591·2	$^2\overline{P}_1-d_1$	T.
3302·55	1·5	30270·9	......	T.
3361·23	1	29742·5	......	T.
3382·28	1	29557·4	......	T.
3397·29	5 R	29426·8	$^2D_3-D_2$	O., 3397·21.
3402·80	3	29379·2	$^2D_3-C_3$	T.
3405·63	7 *u*	29354·7	$^2\overline{P}_1-I_2$	O., 3405·23.
3510·96	6 *u*	28474·2	$^2D_3-B_2$	O., 3510·85.
3519·18	3	28407·6	......	T. [Tl. ?].
3596·11	3 R	27799·9	$^2\overline{P}_1-H_2$	
3599·94	1	27770·4	......	T.
3619·37	2	27621·3	......	T.
3775·75	1	26477·34		

TABLE I. (*continued*).

λ_{air} I. A.	Int.	vac.	Classification.	Remarks.
3887·94	2	25713·3	$^2\overline{P}_1-F_1$	
3888·22	2	25711·4	$^2\overline{P}_1-F_1$	
3912·90	1	25553·2		
4116·35	1	24286·5	......	T.
4121·52	5	24256·1	$^2\overline{P}_1-E_1$	
4121·84	5	24254·2	$^3\overline{P}_1-E_1$	
4127·36	1 *u*	24221·8	......	T.
4220·83	2	23685·3	......	T.
4254·15	1	23499·9	$^4\overline{P}_1-\xi$	$\xi=2475$.
4260·06	1 U	23467·3	......	T.
4308·17	4	23205·2	$^2\overline{P}_1-D_2$	
4308·53	4	23203·3	$^2\overline{P}_1-D_2$	
4492·61	1	22252·6	$^2\overline{P}_1-B_2$	
4492·97	1	22250·8	$^2\overline{P}_1-B_2$	
4615·15	1	21661·7	$\left.\right\}$ $^4S_2-{}^2P_1$	
4615·60	1	21659·6		
4692·32	1 *u*	21305·5	$^4\overline{P}_1-\phi$	$\phi=4670$.
4716·38	1	21197·8	......	T.
4722·19	10	21170·7	$^2D_2-{}^4P_1$	
4722·54	10	21169·1	$^2D_2-{}^4P_1$	
4722·83	10	21167·8	$^2D_2-{}^4P_1$	
4728·96	1	21140·4	......	T.
4733·78	2 *r*	21118·9		
5298·36	1 *u*	18868·5		
5552·23	7 *r*	18005·8		
5599·41	3	17854·1	$^2\overline{P}_2-I_2$	
5718·81	2	17481·3		
5742·59	3 *r*	17408·9		
6134·86	2	16295·8	$^2\overline{P}_2-H_2$	
6184·99	2 U	16163·7		
6364·75	1 *u*	15707·2		
6475·73	3	15438·0	$\left.\right\}$ $^4S_2-{}^2D_3$	
6476·24	3	15436·8		
6991·12	4 *u*	14299·9		
7036·15	2	14208·4	$^2\overline{P}_2-F_1$	
7335·01	1	13629·5		
7441·25	1 *u*	13434·9		
7502·33	2	13325·5		
7838·70	3	12753·7		
7840·33	2	12751·1	$^2\overline{P}_2-E_1$	
8210·83	16	12175·7	$B_2-\xi$	$\xi=2475$.
8501·8	1 U	11758·99		
8544·54	2	11700·2	$^2\overline{P}_2-D_2$	

TABLE I. (*continued*).

λ_{air} I. A.	Int.	$\nu_{vac.}$	Classification.	Remarks.
8579·74	1	11652·2	${}^2P_2-C_3$	
8627·9	1 U	11587·1		
8754·88	2	11419·1	${}^4S_2-{}^2D_2$	
8761·54	3	11410·4		
8907·81	2	11223·0	$D_2-\xi$	$\xi=2475$.
9058·62	1	11036·2		
9342·60	1 *u*	10700·7		
9657·2	300	10352·1		

$\lambda_{Rowland.}$	Int.	$\nu_{vac.}$	Classification.	Remarks.
9828·8	20	10171·4	$E_1-\xi$	$\xi=2475$.
10106·1	20	9892·3		
10301·7	15	9704·5		
10540·2	8	9484·9		
11073·2	15	9028·4	$D_2-\phi$	$\phi=4670$.
11555·5	5	8651·5		
11711·1	100	8536·6		
11994·5	13	8334·9		
12166·5	40	8217·1		
12690·5	30	7877·8		
14331·5	25	6975·7		
2254·2	7	4432·6	$H_2-\phi$	$\phi=4670$.

Theoretical Considerations.

Bismuth belongs to the group of five-valence elements (N, P, As, Sb), and it may be recalled that the spectra of none of these elements have been completely elucidated. Fowler * has classified the lines of O^+, but he could not trace the fundamental levels. Millikan and Bowen † have discovered some of the fundamental levels of O^+ in the extreme ultra-violet, but the mutual relationship between the intercombination systems has not yet been completely established. A discussion of the structure of the spectrum of O^+ from the standpoint of Hund's theory has been given by R. H. Fowler and D. Hartree ‡.

* A. Fowler, P. R. S. (Lond.) A, vol. cx. p. 476 (1926).

† Millikan and Bowen, 'Nature,' Sept. 1926, p. 410.

‡ R. H. Fowler and D. Hartree, P. R. S. (Lond.) A, vol. cxi. p. 83 (1926). For nitrogen, see Kiess, Journ. Opt. Soc. Am. July 1925. For phosphorus, Saltmarsh, Phil. Mag. vol. xlvii. p. 874 (1924).

Let us begin with the electronic composition of Bismuth. It may be written as :—

$$
\begin{tikzcd}[row sep=small]
2\,K & 8\,L & 18\,M & 32\,N & & \\
 & \begin{matrix}O_1\\2\end{matrix} & \begin{matrix}O_2\\6\end{matrix} & \begin{matrix}O_3\\10\end{matrix} & O_4 & \\
 & & \begin{matrix}P_1\\2\end{matrix} & \begin{matrix}P_2\\3\end{matrix} \arrow[r] \arrow[d] & P_3 \arrow[d] & P_4 \\
 & & & Q_1 \arrow[r] & Q_2 \arrow[d] & Q_3 \\
 & & & & R_1 & R_2
\end{tikzcd}
$$

[For detailed explanation, see a paper by Kichlu and Saha, "On the Explanation of Anomalous Terms in the Spectra of Two-Valence Elements" (Phil. Mag. July 1927).]

The letters K L M N O denote the X-ray levels, and the numbers under them represent the number of electrons in that level. Possible transitions giving rise to line spectra are indicated by arrows.

The combinations and expected terms are shown below :—

$$
\begin{tikzcd}[column sep=small]
 & \begin{matrix}2\,P_2\,Q_1\\ {[{}^4P,\ {}^2P,\ {}^2\overline{D},\ {}^2\overline{S}]}\end{matrix} \arrow[dr] & \\
\begin{matrix}3\,P_2\\ {[{}^1S_2,\ {}^2D_{2,3}\ {}^2\overline{P}_{1,2}]}\end{matrix} \arrow[ur] \arrow[dr] & & \begin{matrix}2\,P_2\,Q_2\\ \left[\begin{matrix}{}^4D,\ {}^4\overline{P},\ {}^4S\\ {}^2D,\ {}^2P,\ {}^2S\end{matrix}\right]\\ \text{etc.}\end{matrix} \\
 & \begin{matrix}2\,P_2\,P_3\\ \left[\begin{matrix}{}^4F,\ {}^4D,\ {}^4P\\ {}^2F,\ {}^2D,\ {}^2P\end{matrix}\right]\\ \text{etc.}\end{matrix} \arrow[ur] &
\end{tikzcd}
$$

Explanation.—$3\,P_2$ indicates that all the 3-valence electrons are at P_2-level. $2\,P_2\,Q_1$ indicates that one has gone over to Q_1 etc. The terms arising from any combination, as calculated according to the theory of structure of complex spectra, are shown below that combination. Attention is drawn to the fact that in the symbols $3\,P_2$, $2\,P_2\,Q_1$, ${}^2P_2\,P_3$, etc., P indicates the particular shell in the atom numbered according to the convention, K, L, M, ... But ${}^2P_{1,2}$ etc. in the brackets indicate spectral terms having P-characteristics. The confusion is regretted, but is unavoidable.

Bismuth being a heavy element will show abnormally wide separations in the values of the terms arising from the same electronic combination. I have therefore started with the theoretical spectrum of Bi^+, of which the fundamental levels are ${}^3P_{0,1,2}$, ${}^1\overline{D}_2$, ${}^1\overline{S}_0$. To calculate the terms of Bi,

I have taken each one of these optical levels, and brought a fresh electron to each of the outer levels, and calculated the possible orbits. This is shown in Chart I., and then the range in value of the terms is discussed below, and their identification is carried out in Table II.

CHART I.

$2P_2Q_1$ Combination.	j-value.	Landé's "j".	Terms.	Identification.
$(^3P_0)\ ^2S_{1/2}$	1/2	1	$^4P_1$	A_1
$(^3P_1)\ ^2S_{1/2}$	1/2	1	$^2P_1$	E_1
	3/2	2	$^4P_2$	D_2
$(^3P_2)\ ^2S_{1/2}$	3/2	2	$^2P_2$	H_2
	5/2	3	$^4P_3$	G_3
$2P_2P_3$ Combination.	j-value.	$j+1/2$.		
$(^3P_0)\ ^2D_{3/2},\ _{5/2}$	3/2	2	X_2	B_2
	5/2	3	X_3	C_3
$(_3P_1)\ ^2D_{3/2},\ _{5/2}$	1/2	1		
	3/2	2	...	I_2
	5/2	3	...	J_3
	3/2	2		
	5/2	3		
	7/2	4		
$(^3P_2)\ ^2D_{3/2},\ _{5/2}$	1/2	1		
	3/2	2		
	5/2	3		
	7/2	4		
	1/2	1		
	3/2	2		
	5/2	3		
	7/2	4		
	9/2	5	$^4F_5$	

TABLE II.

	$^4S_2$.	$^2D_2$.	$^2D_3$.	$^2P_1$.	$^2P_2$.	Term value.
$2P_2Q$. A $(^3P_0)\ ^2S_{1/2} \rightarrow {}^4P_{1/2}$	32587·9 3067·73 (10 R)	21170·7 21169·1 21167·8 4722·12 (10) 4722·54 (10) 4722·83 (10)	……	(10927)	$-ve$	25975
$2P_2P_3$ B $(^3P_0)\ ^2D_{3/2}$ 3/2	43912·2 2276·57 (10 R)	32493·0 3076 69 (2 R)	28474·2 3510·96 (6 *u*)	22252·6 22250·8 4492·61 (1) 4492·97 (1)	(10745)	14650
$2P_2P_3$ C $(^3P_0)\ ^2D_{5/2}$ 5/2	44816·4 2230·64 (10 R*u*)	33397·5 2993·36 (6 R)	29379 2 T 3402·80 (3)	……	11652·2 8579·74 (1)	13746
$2P_2Q_1$ D $(^3P_1)\ ^2S^1/_2$ $^4P_{3/2}$	44864·6 2228·23 (10 R)	33445·8 2989 05 (7 R)	29426·8 3397·29 (5 R)	23205·2 23203·3 4308·17 (4) 4308·53 (4)	11700·2 8544·54 (2)	13698
$2P_2Q_1$ E $(^3P_1)\ ^2S_{1/2}$ $^2P_{1/2}$	45915·7 2177·22 (4 R)	34496·6 2897·99 (9 R)	……	24256·1 24254·2 4121·52 (5) 4121·81 (5)	12751·1 7840·33 (2)	12647
$2P_2R_1$ F 1/2	47371·3 2110·31 (10 R)	35953·9 2780·52 (8 R)	……	25713·3 25711·4 3887·94 (2) 3888·22 (2)	14208·4 7036·15 (2)	11190
$2P_2Q_1$ G $(^3P_2)\ ^2S_{1/2}$ $^4P_{5/2}$	48488·1 2061·70 (10 R)	37070·5 2696·76 (6 R)	33052·0 3024·67 (7 R)	……	(15326)	10073
$2P_2Q_1$ H $(^3P_2)\ ^2S_{1/2}$ $^2P_{3/2}$	49459·3 2021·21 (6 R)	38041 6 2627·92 (8 R)	34023·1 2938·32 (9 R)	27791·9 3596·12 (3 R)	16295·8 6134·86 (2)	9102
$2P_2P_3$ I $(^3P_1)\ ^2D_{3/2}$ 3/2	51017·3 1959·48 (8 R)	39599·5 2524·53 (9 R)	35581·4 2809·64 (6 R)	29354·7 ? 3405·63 (7 *u*)	17854·1 5599 41 (3)	7544
$^2P_2P_3$ J $(^3P_1)\ ^2D_{5/2}$ 5/2	51163·2 1953·89 (8 R)	39738 7 2515 68 (9 R)	35719·8 2798·74 (6 *u*)	……	(17993)	7405
$2P_2R_3$ K 3/2	(53975)	42556·5 T 2349·10 (3)	38538·6 2594·03 (1)	32315·7 T 3093·58 (5 *u*)	(20810)	4587
L 3/2	(56569)	45150·7 2214·11 (3 R)	41132·1 2430·45 (3 *u*)	34905·8 2864·01 (7 *u*) ?	(23406) ?	1993
M 5/2	(57057)	45656·6 2189·59 (8 R)	41638·4 2400·90 (10 R)	……	(23912) ?	1487
N 3/2	(58271)	46852·3 2133·68 (6 R)	42835·6 2333·79 (7)	36613·2 2730 45 (6 *u*)	(25109) ?	291
a ? 5/2	43205·6 T 2313·8 (1 R)	31791·4 ? T 3144·6 (5 U)	27770·35 T 3599·94 (1)			
b 3/2	(64019)	(52601)	48582·8 T 2057·68 (5)	42358·1 2360·1 (1 U)	30854·8 T 3239·73 (5)	
c 3/2	(66102)	(54684)	50665·7 1973·08 (5)	44442·9 T 2249·38 (5)	32937·5 T 3035·18 (3 *u*)	
$2PS_1$ *d* 1/2	52252 1902·6 (2 R)	40832·3 2448·30 (8 *r*)	……	30591·2 T 3267·97 (1 *u*)	(19086)	

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(a) *The Fundamental Levels.*

Five fundamental levels are expected—$^4S_2$, $^2D_{2,3}$, $^2P_{1,2}$. It is natural to identify them with the levels discovered by Kayser and Runge, but several discrepancies have to be removed.

A glance at Table II. shows that the first two levels have the same combinatory powers up to the sublevel denoted by "J." The only discrepancy was in the level E. There are two close lines, λ 2177·22 and λ 2176·62, and, according to Ruark etc., it is the shorter line which is the more intense and more easily absorbed. But my measurements show that the longer line, λ 2177·22, is the more intense and is always obtained in absorption, while λ 2176·62 appears very faintly on one plate only. With this correction, E fits in well under both levels.

Beyond this level the lines which arise from combination with $^4S_2$ fall in the Schumann region. Bloch has given data for this region, but they do not seem to be reliable.

The third level has the j-value $=3$, for it gives fewer combinations. I have specially looked for the lines ($^2D_3-E$) and ($^2\bar{P}_1-C$), but they are definitely absent.

The close levels "$^2\bar{P}_1$" having the separation 1·91 have probably the same inner quantum number 1, and differ only in the "fine quantum number" introduced by Ruark *.

I have provisionally identified the fifth level $^2\bar{P}_2{}'$ with Ruark's "β". This is a bit doubtful.

(b) The next level arise from the combinations

$$\left.\begin{array}{l} 2\,P_2\,Q_1 \\ 2\,P_2\,P_3 \end{array}\right\} .$$

We have to identify these levels with the levels denoted by A_1, B_1, C_1, etc., and a mere glance at the chart shows that there is a wide divergence in the scale of values of these terms. We are here encountering terms of the "displaced type," first discovered by Paschen in the spectrum of Neon †, and since confirmed by Grotrian ‡ and Sur §

* Ruark, Phil. Mag vol. l. p. 937 (1925); Sommerfeld, Three Lectures on Atomic theories, p. 12.

† Paschen, *Ann. der Physik*, vols. lx. and lxiii.

‡ Grotrian, *Zeits. für Physik*, vol. xxxix.

§ Sur, "On the Spectrum of Pb" (Phil. Mag.); Meissner, *Zeits. für Physik*, vol. xl.

in the spectrum of Pb. We shall take the discussion of this point in detail.

The fundamental terms of Bi^+ are given by the combination $^2P_2$ giving us the terms

$$^3P_0 \qquad ^3P_1 \qquad ^3P_2 \qquad ^1D_2 \qquad ^1S_0$$

similar to those of lead. In the case of lead,

$$^3P_0 - {}^3P_1 = 7817,$$

$$^3P_1 - {}^3P_2 = 2813.$$

In the case of Bi^+, we assume that

$$^3P_0 - {}^3P_1 = 16,000,$$

$$^3P_1 - {}^3P_2 = \ \ 6,000.$$

When we form Bi by bringing another electron, either in position Q_1 or in P_3, it is comparatively lightly coupled to the inner electrons. We can classify the new terms from $(2\,P_2\,Q_1)$, and $(2\,P_2\,P_3)$ in three groups, viz. (1) from $^3P_0$-state, (2) from $^3P_1$-state, (3) from $^3P_2$-state of Bi^+; and we expect that these groups are approximately separated by the values $^3P_0 - {}^3P_1$, $^3P_1 - {}^3P_2$. These three groups are shown in the tabulated form in Chart I. (p. 782).

In calculating the resultant J-values, we have assigned the Sommerfeld "j"-values to each term. This is shown in column 2. In column 3 the conventional, or Landé j-values, are given. This is Sommerfeld's $(j+\frac{1}{2})$.

It will be seen that we get three terms from $^3P_0$-level, viz. $^4P_1$ and X_2, X_3. In analogy with Pb, since $^4P_1$ arises from the electron configuration $(2\,P_2\,Q_1)$, we may assign to $^4P_1$ the approximate value $\frac{N}{2^2}$, and to X_2, X_3 the value $\frac{N}{3^2}(2\,P_2\,P_3)$. We have therefore no difficulty in identifying $^4P_1$, X_2, X_3 with A, B, C, respectively.

The $(^3P_1)\,^2S$ terms will be less than $(^3P_0)\,^2S$ or $^4P_1$ by about 16,000. Hence we may identify these as :—

$$D = {}^4P_2, \qquad E = {}^2P_1.$$

The $(^3P_1)\,^2D$-terms will be very small, or may even be negative.

The terms arising from $(^3P_2)\,_2S$ can be easily identified

with G and H. The inner quantum numbers are in perfect agreement.

These identifications leave out the term F with $j=1$, and Thorsen is therefore justified in identifying it as the higher Rydberg member of $^4P_1$ or A, *i. e.* as $(2\,P_2\,R_1)$.

In Table III. we give lines which probably form a Rydberg sequence.

TABLE III.

	$^4S_2$.	$^2D_2$.	$^2P_1$.	$^2P_2$.
	3067·73 (10 R) 32587·9	4722·54 (10 R) 21169·1	(10927) ?	Negative.
X_1	2110·31 (10 R) 47371·3	2780·52 (8 *r*) 35953·9	3887·94 (2) 25713·3	7036·15 (2) 14208·4
		2448·30 (8 *r*) 40832·3	3267·97 (1 *u*) 30591·2	(19086) ?

The lines under the heading $^2D_2$ are given by the Hicks's formula :—

$$\nu = 47143 - \frac{N}{\left(m + \cdot 28143 - \frac{\cdot 45324}{m}\right)^2}$$

$$m = 2, 3, 4.$$

Thorsen gives $^2D_2 = 47323$. It is due to the fact that he gave the third row incorrectly. The line λ 3267·97 predicted by Thorsen appeared on my plates. The first line of the 3rd row is given by Thorsen as λ 1913·5. Dr. Sur has always got the line λ 1909·6 in absorption. I have been unable to identify the higher members predicted by Thorsen, or members arising from my formula.

The terms arising from $(^5P_0)\,^2D_{3/2}$, viz. in the electron configurations $2\,P_2\,(P_3)$, $2\,P_2\,(Q_3)$, $2\,P_2\,(R_3)$... will form a regular Rydberg sequence. The lines provisionally identified are shown in Table IV.

TABLE IV.

	$^4S_2$.	$^2D_2$.	$^2D_3$.	$^2P_1$.
X_2	λ 2276·57 (10 R) 43912·2	λ 3076·69 (2 R) 32493·0	λ 3510·96 (6 *u*) 28474·2	(22252·6)
	λ 1959·48 (8 R) 51017·3	λ 2524·53 (9 R) 39599·5	λ 2809·64 (6 R) 35581·4	λ 3405·63 29358·2
	(53975)	λ 2349·10 (3) 42556·5	λ 2594·03 (1) 38538·2	λ 3039·58 (5 *u*) 32315·7

The lines under $^2D_2$ can be represented by the formula

$$\nu = 47314 - \frac{N}{\left(m - \cdot 08059 - \frac{\cdot 59766}{m}\right)^2},$$

$m = 3, 4, 5.$

It is seen that the limits calculated from both sets come almost to the same value.

Table V. shows the lines which form a regular Rydberg sequence with terms X_3 arising out of combination $^3P_0\,^2D_{5/2}$.

TABLE V.

	$^4S_2$.	$^2D_2$.	D_3.	Term value.
X_3	44816·4 λ 2230·64	33397·5 λ 2993·36	29379·2 λ 3402·80	13746
	51163·2 λ 1953·89	39738·7 λ 2515·68	35719·8 λ 2798·74	7405
	(54032)	42614 λ 2345·91	(38596)	4529

The lines under $^2D_2$ may easily be grouped under a Rydberg sequence. The last term is somewhat doubtful.

No regular Rydberg sequence except these three is expected. The terms arising out of $^3P_1$ or $^3P_2$ will form regular sequences if 16,000 and 6000 approximately are added to them. Hence all terms after the first will become very small or negative. Unless the spectrum is investigated in the Fluorite region, it will be difficult to identify them.

Lines occurring as the result of intercombination between the states $2\,P_2\,P_3$, $2\,P_2\,Q_2$ and $2\,P_2\,Q_1$, $2\,P_2\,Q_2$ have been looked for from the existing data, but only the following have been found :—

λ.	ν.	
4254·15	23499·9	A_1-2475
8210·83	12175·7	B_2-2475
8907·81	11223·0	D_2-2475
9828·8	10171·4	E_1-2475

The above was found by Ruark and others; in addition I find the one given below :—

λ.	ν.	
4692·32	21305·5	A_1-4670
11073·2	9028·4	D_2-4670
2254·2	4432·6	H_2-4670

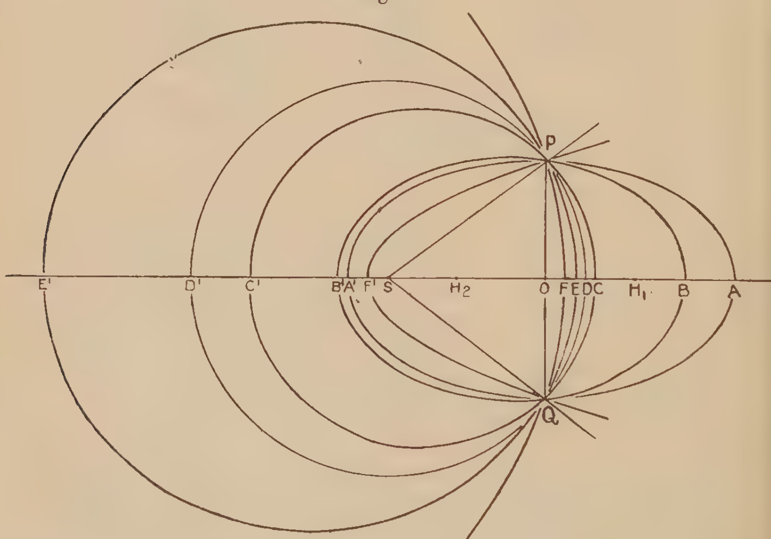
It seems that the existing data are not sufficient to establish the intercombination terms, and hence the region λ 4800 to λ 8000 is now being investigated.

In conclusion, I wish to thank Prof. M. N. Saha, under whose direction and guidance this investigation has been carried on. I am also much obliged to Dr. N. K. Sur for his supplying me with some of his unpublished data on Bismuth under-water spark and absorption spectra of Bismuth.

LXX. *On the Action in Planetary Orbits.* By W. B. MORTON, *M.A.*, *and* W. W. BRUCE, *M.Sc.*, *Queen's University, Belfast* *.

IN a note which appeared in this Magazine in October 1926 † the variation of the action was examined arithmetically for the parabolic trajectory under constant gravity between two points at the same level. In the present note the same thing is done for the path under the law of the inverse square between points at equal distances from the centre of force. The guided paths, like the free ones, are taken to be conics with the centre of force in a focus, and the terminal velocity is kept constant, so that the principle of least action is illustrated.

Fig. 1.



There are four free paths from P to Q in presence of the centre S (fig. 1), forming two ellipses BB′, CC′. These have the same length of major axis, so, if H_1H_2 are their empty foci, $PH_1 = PH_2$. The focal chords PH_1, PH_2 intersect the paths again in the segments PBQ, PC′Q, so the other segments PB′Q, PCQ are those which have minimum action.

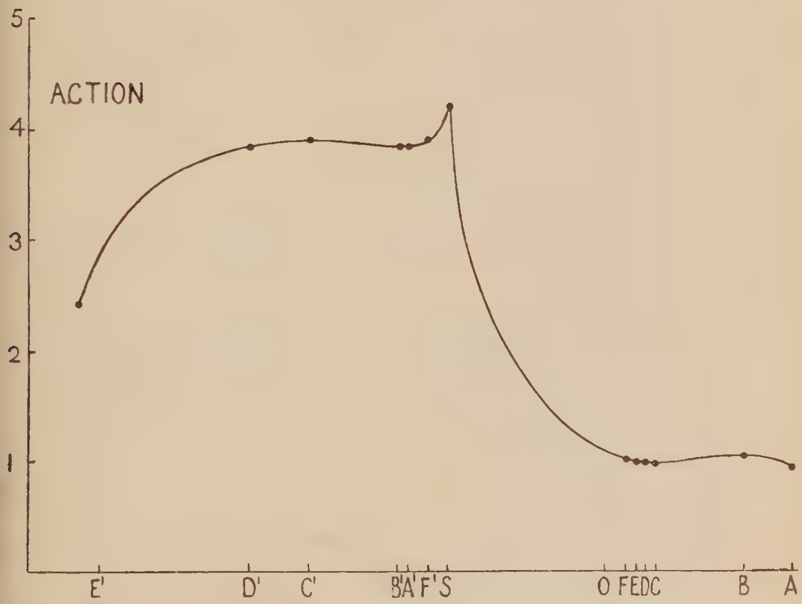
* Communicated by the Authors.

† W. B. Morton, "On the Action in Parabolic Paths under Gravity," Phil. Mag. ii. p. 800 (1926).

It will appear that, with the mode of variation here adopted, the action along the paths by B, C′ has a maximum value.

It is evident that as the vertex of the guided path moves from B′ to C, through a series of conics with focus at S and passing through PQ, the action must pass somewhere through a maximum, and yet there is no such path for which the variation of the action vanishes in the ordinary sense. The maximum occurs when the conic becomes the pair of lines SP, SQ, and the paradox is explained by the discontinuity in the direction at S when we pass from the line-pair to a near hyperbola. There is a corresponding discontinuity in

Fig. 2.



direction on the curve (fig. 2), in which action is plotted against the position of the vertex of the path.

The species of the conics with which we have to deal are most readily determined by reference to the two orthogonal parabolas F, F′. When the vertex of the curve lies outside the segment FF′, the conic is an ellipse; when it lies within FF′, a hyperbola. The line PQ is a special hyperbola with vanishing transverse axis, the other focus being the image of S in the line.

The possible elliptic guided paths are limited by the

magnitude of the velocity given to the particle at P; it cannot get further from S along any path than a definite maximum distance at which its kinetic energy is all used up in work against the attraction. There are thus two limiting ellipses (AA′, EE′ on fig. 1) having this distance as their maximum radius vector on either side of S.

The special case represented on fig. 1, and worked out numerically in what follows, is that in which the triangle SPH_1 is right-angled, with sides as 3 : 4 : 5. It was chosen for the sake of round numbers. It corresponds to a kinetic energy of the particle at P, which is $\frac{3}{7}$ of that which would be gained by a fall from infinity to P. The greatest distance attainable is thus $\frac{7}{4}\mathrm{SP}=\mathrm{SA}=\mathrm{SE}$.

It is easy to express the action-integral in terms of the coordinate r. Let μ be the strength of the centre, $2a_0$ the major axis of the free paths, $2a$, γ, δ the major axis, greatest radius, and least radius of one of the guided elliptic paths. Then we find

$$\mathrm{A}=\int_{\mathrm{P}}^{\mathrm{Q}} v\,ds=2\sqrt{(\mu/a_0)}\int(2a_0-r)^{\frac{1}{2}}(2a-r)^{\frac{1}{2}}(\gamma-r)^{-\frac{1}{2}}(\delta-r)^{-\frac{1}{2}}.dr$$

taken between P and the vertex of the ellipse.

The hyperbolic paths fall into two classes with slightly differing expressions for A:—

(1) Those for which S is on the concave side, with vertices between F and O or between S and F′. Then

$$\mathrm{A}=2\sqrt{(\mu/a_0)}\int(2a_0-r)^{\frac{1}{2}}(r+2a)^{\frac{1}{2}}(r+\gamma)^{-\frac{1}{2}}(r-\delta)^{-\frac{1}{2}}.dr.$$

(2) Those for which S is on the convex side, vertices between O and S,

$$\mathrm{A}=2\sqrt{(\mu/a_0)}\int(2a_0-r)^{\frac{1}{2}}(r-2a)^{\frac{1}{2}}(r-\gamma)^{-\frac{1}{2}}(r+\delta)^{-\frac{1}{2}}.dr.$$

There are five special cases in which the integral can be expressed by circular functions:—

(1) The limiting paths. Here $\gamma=2a_0$,

$$\int=2a_0\sin^{-1}\sqrt{\{(r-\delta)/(2a-\delta)\}}+(r-\delta)^{\frac{1}{2}}(2a-r)^{\frac{1}{2}}.$$

(2) The free paths, $a=a_0$,

$$\int=2a_0\sin^{-1}\sqrt{\{(r-\delta)/(\gamma-\delta)\}}+(\gamma-r)^{\frac{1}{2}}(r-\delta)^{\frac{1}{2}}.$$

(3) The circular path, when $\mathrm{A}=v\times\mathrm{arc}$.

(4) The parabolic paths. Here $2a$ and γ become infinite with a ratio of equality and δ is the parameter,

$$\int = (2a_0-\delta)\sin^{-1}\sqrt{\{(r-\delta)/(2a_0-\delta)\}} + (2a_0-r)^{\frac{1}{2}}(r-\delta)^{\frac{1}{2}}.$$

(5) The degenerate hyperbola, which consists of the two straight lines SP, SQ,

$$\int = 2a_0\sin^{-1}\sqrt{(r/2a_0)} + r^{\frac{1}{2}}(2a_0-r)^{\frac{1}{2}}.$$

By these formulæ we obtain values of the action for the thirteen positions of the vertex A B C D E F S F′A′B′C′D′E′. For intermediate points the action can be expressed by elliptic functions; but, as is usual in physical questions, the "integrals of the third kind" have an imaginary parameter, and calculation from the formulæ is very laborious. For our purpose it is much simpler to apply arithmetical quadrature to the original formulæ in r. This was done for twenty-two positions of the vertex of the guided path and the graph (fig. 2) plotted from the results. Afterwards, by way of verification, and as an exercise in computation, the elliptic formulæ were used for two points, one between B, C and the other between B′, C′, chosen so as to give an even value for the modular angle. The points so obtained were found to lie exactly on the curve.

The thirteen special points are marked on the graph, and the axis of abscissæ lettered to correspond.

The unit marked on the vertical axis is the action along the short circular arc from P to Q. It will be noticed that, as in the former case of the parabolic trajectory, the range between the minima C, B′ and the maxima B, C′ is very small.

The values found for the action at these points are:—

B	1·052,	B′	3·882,
C	·997,	C′	3·936.

An attempt was made to establish analytically the nature of the stationary values of the Action. The length γ was taken as the independent variable. It was not difficult to show that $dA/d\gamma$ vanishes for the free paths, but the expression for the second differential proved too cumbrous for handling.

LXXI. *On the Surface Tension of Rock-Salt.*

By G. N. ANTONOFF, *D.Sc.* (*Manch.*) *.

THERE is comparatively little known about surface tension of solids, chiefly owing to the want of a suitable method of determining the same. The subject, however, presents an enormous theoretical and practical interest. In its theoretical aspect the knowledge of the surface tension is of importance, because it may throw light on internal structure of solids.

One can say that up to now very little work has been done on the subject. Moreover, up to quite recently the very notion of the surface tension of solids was so vague that one could doubt whether it had any real meaning. Thus, for example, in Chwolson's 'Traité de Physique,' p. 612 (1906–8), it is assumed that water vapour must have condensed on the walls of the solid to account for its surface tension.

The impetus for the development of this important subject, one may say, was laid down by the work of P. Curie (*Bull. Soc. Min. de France*, viii. p. 145, 1885; also 'Œuvres,' p. 153). His ideas were very much ahead of his time, and with his premature death they did not find any immediate following, having fallen, so to say, on unprepared ground. Very little work of importance has been done on the subject until quite recently. The literature of the subject can be found, summarized up to 1915, by P. Ehrenfest, *Ann. d. Phys.* (4) xlviii. p. 360 (1915).

And only recently an attempt was made by Max Born to estimate the surface tension of rock-salt, under the assumption that it consists of positive and negative ions held up in equilibrium by purely electrical forces.

These results are described in a paper by M. Born and O. Stern (*Sitz. Preuss. Akad. Wiss.* xlviii. p. 901, 1919). Apart from attractive forces, they assume the existence also of repulsive forces, as a result of experimental evidence regarding the compressibility of rock-salt under external pressure.

In this work it is assumed that the structure of rock-salt is such as revealed by the X-ray analysis.

The surface tension of rock-salt, calculated under the

* Communicated by the Author.

above assumption, was found to be at the absolute zero of temperature

$$150 \cdot 2 \text{ erg cm.}^{-1} \text{*}.$$

Taking into consideration that at the melting-point (above 800° C.) the surface tension of the molten salt is about

$$65 \cdot 5 \text{ erg cm.}^{-1},$$

the surface tension at ordinary temperature will be about

$$125 \text{ erg cm.}^{-1},$$

assuming that the surface tension is roughly a linear function of temperature.

It may appear at first sight that similar results can be attained from the breaking stress of crystals. The breaking stress of rock-salt is a fairly constant figure and is the same along the three principal axes. The estimates of surface tension from the breaking stress lead, however, to a ridiculously low figure (see my paper, Phil. Mag. xliv. p. 62, July 1922). It is quite natural to assume that there are some cracks always present in the crystal.

On the other side there appear to be some doubts as to the actual structure of rock-salt and other substances.

It is known that phenomena of association take place in the liquid state, which makes it probable that something similar will also apply to the solid state. Thus it was stated by Sir William H. Bragg ('Nature,' cxi. p. 428) that the ultimate unit of crystal structure or elementary parallelepiped is not a chemical molecule, but is a complex formed by the union of a number of molecules. Or else, the surface structure of the crystal must be different from that at the interior.

The recent work of the writer of this paper (Phil. Mag. March 1927) indicates that molecular association in the liquid state with the decrease of temperature proceeds in definite stages according to the law of multiple proportions, and the association factor must reach a very high value by the time the substance becomes solid.

It thus appears that it is not safe to calculate the surface tension on a basis of a theory involving the molecular structure of crystals.

For this reason I made it a point of evolving a method which would give a measure of the molecular field in a more or less direct way.

* According to my usual notations it should be dynes cm.$^{-1}$. See paper by Ph. A. Guye, Journ. Chem. Phys. 5, p. 427 (1907).

Such experiments were already described by myself in my paper (Phil. Mag. June 1926), where I give as a figure for surface tension of glass

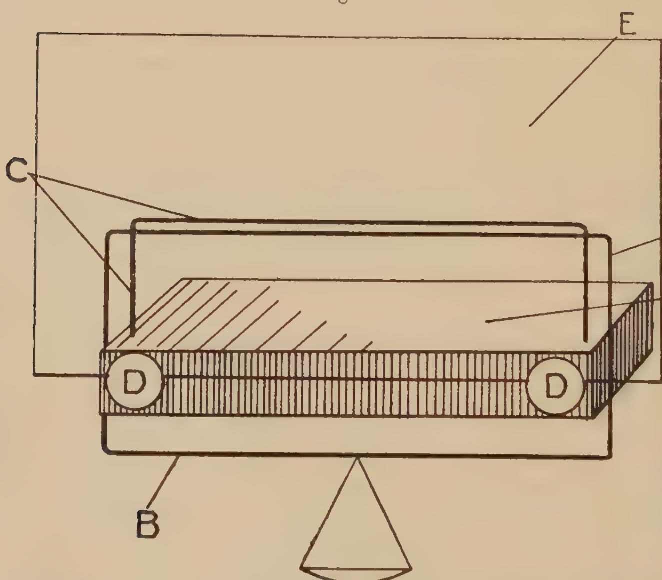
130 dynes per cm.

Now I intend to describe a modified method, which is more suited for measuring the surface tension of rock-salt, and to put forward some theoretical considerations indicating that the constants obtained by *my method do actually represent the surface tension.*

The Method and its Theory.

The method consists in preparing suitable pastes * whose surface tensions can be measured by determining the breaking stress of their films. The apparatus used for this purpose is seen on fig. 1. A small table A bears a horizontal rod C

Fig. 1.



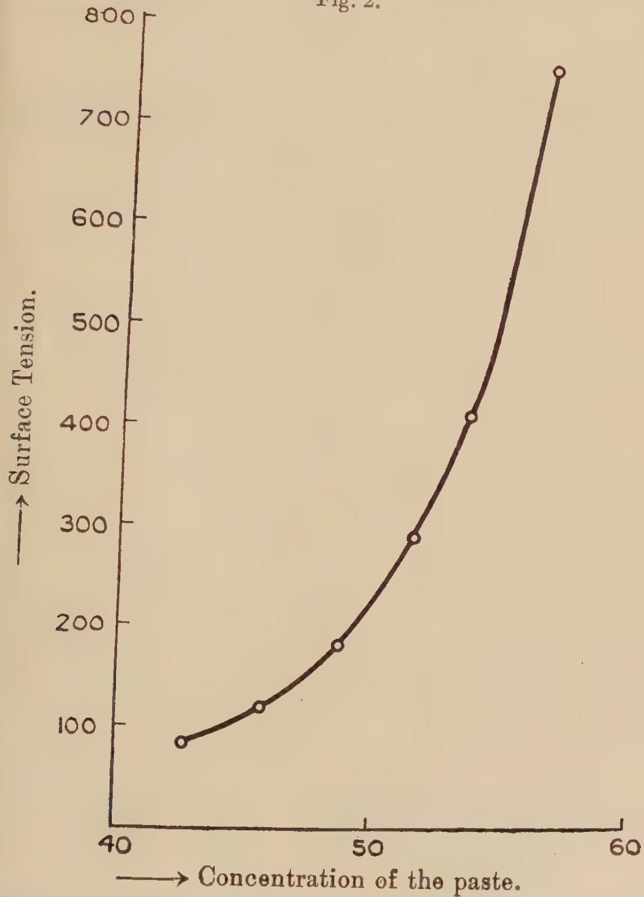
made of thin glass with two ends bent at right angles, fixed in its horizontal surface. Another glass rod B is bent into a quadrangle bearing the tray for weights. The horizontal part of C with the upper horizontal part of B are kept together by the paste used, and B falls on the table when

* Phil. Mag. p. 1263, June 1926.

the applied weight exceeds the breaking stress of the film. The frame B is of length exceeding that of table, so that there is no contact between them and no friction during the fall of B.

The vertical front part of the table bears two drawing pins D holding a glass E in front of the apparatus to protect it from breath, as moisture seriously affects the result.

Fig. 2.



The pastes of different concentrations have surface tensions as shown in the drawing (fig. 2).

These pastes are used for determining the surface tension of solids in the following way :—

A tube is taken of material whose surface tension is to be

measured, and the pastes of different concentration are pressed through the same.

It can be seen that the more dilute pastes passing through the tube leave a thin film on the walls of the solid—they wet its surface.

However, as soon as the surface tension of the paste used reaches a certain value, the paste ceases to wet the wall and leaves the tube without adhering to its surface.

The same constant appears in experiments where pastes are made of different constituents.

It appears highly probable that unless other factors intervene, such as solubility or chemical actions, these facts must be connected with surface tension of the solid in some way or another.

This can be made clear in the following way (see fig. 3).

Fig. 3.

In this figure the Medium I represents the solid (glass, rock-salt, etc.), the Medium II the paste, and the Medium III can be disregarded altogether, as representing the air or vacuum.

The notations used are as follows :—

α_1 —the surface tension of the solid (against vacuum or air).

α_{12}—the tension at the interface solid-paste.

α_2 —the surface tension of the paste (against vacuum or air).

According to the elementary theory the following equation must hold true when three media are in contact with one another (see Chwolson, 'Traité de Physique,' p. 612, 1906–8):

$$\cos\theta = \frac{\alpha_{1,3} - \alpha_{1,2}}{\alpha_{2,3}}.$$

Considering that the Medium III can be left out of consideration in this problem, the same expression in our notations will be:

$$\alpha_2 \cos \theta = \alpha_1 - \alpha_{12}.$$

In the experiments described in this paper the angle θ has always increasing values until it reaches 90° at the transition point to be located by these experiments. At this point $\cos \theta$ becomes $=0$, and consequently

$$\alpha_1 = \alpha_{12}.$$

The actual meaning of these experiments is as follows:—

When the interfacial tension is greater than that of the paste, *i. e.*

$$\alpha_{12} > \alpha_2,$$

the paste adheres to the wall of the solid.

When on the contrary

$$\alpha_{12} < \alpha_2,$$

the paste ceases to wet the solid.

At the transition point

$$\alpha_{12} = \alpha_2,$$

but we have also seen that at the transition point, when $\cos \theta = 90°$,

$$\alpha_1 = \alpha_{12}.$$

It therefore follows that in these conditions the *surface tension of the paste is equal to that of the solid.*

$$\alpha_2 = \alpha_1.$$

It thus appears that the constant obtained by these experiments in this sense is nothing else but the surface tension of the solid itself.

Now it remains to define the actual conditions under which such experiments must be performed.

In my previous paper I did not make any mention of the diameter of the tube to be used.

I found from experience that the tube of the solid must not be too wide.

I take a crystal of rock-salt and bore a hole in it in the direction of one of its principal axes. As rock-salt belongs to the regular system, it does not matter which direction is chosen for the experiment. The hole can be easily made using an ordinary lathe with water as lubricator. Then a glass tube is taken nearly of the same diameter as the

cylindrical hole, and is joined to the rock-salt by means of a sealing mixture (see fig. 4).

The other end of the glass tube adjoined is drawn into a narrow capillary *. The latter is necessary to create suitable resistance to the flow of the paste under influence of external

Fig. 4.

pressure. All these experiments are difficult because it is not easy to prescribe the exact conditions. If the capillary is too narrow, the resistance may be too big, so as to prevent the passage of the paste almost completely. If it is too broad, the experiment becomes impossible, because the passage takes place instantaneously. The right conditions

* This is not shown on the drawing.

can only be found empirically. I may add that the resistance can be sometimes increased by introducing a bubble of air (or several bubbles) into the tube. When the paste with a bubble of air descends in the tube the bubble will appear translucent or transparent, according to whether the paste wets the wall or otherwise.

A much more important point is, what diameter to choose for the tube of the solid.

If this diameter is too big, the experimental device shown in fig. 4 will not work at all.

The external pressure will not extrude the paste from the tube, but the air will rush through the same, leaving a very narrow channel in the middle of the tube.

I found by experience that diameters of the order of magnitude of ·1 of an inch suit the experiment very well. In the experiments with glass I have varied the diameter within certain limits, and in all cases I did not find that the constant obtained was thereby affected. However, I avoided very narrow tubes in which special conditions may arise which may affect appreciably the experiment.

Using the pastes, as described in my previous paper, in the device shown in fig. 4, I found for rock-salt as the average of several determinations the value

315 dynes per cm.

It must be borne in mind that in this region the curve (fig. 2) is very steep, and therefore small changes of concentration produce an appreciable change in the surface tension of the paste.

Discussion of Results.

(1) The method described is not universal. It is limited to certain ranges of values of surface tension, and it is applicable provided there is no dissolving or chemical action of any kind.

It is applicable to most of the crystalline salts, such as rock-salt etc.

(2) The result obtained does not depend on cracks in the crystal, and is a measure of the molecular field exercised by the solid.

If there are any doubts concerning the molecular structure of the solid, the results obtained are thereby not affected at all.

(3) The figures obtained by the method described repeat themselves invariably. No changes of any kind, due to the

time of contact between the paste and the solid, were noticed in the course of these observations.

(4) The theoretical considerations hereinbefore described indicate that the figures obtained do actually represent the surface tension of the solid.

(5) The figure obtained for rock-salt differs considerably from that calculated by Born, which is to be expected from the point of view of the theory laid down in the number of papers *, indicating that molecules must be highly associated in the solid state.

6 Featherstone Buildings,
High Holborn,
London, W.C. 1.

LXXII. *A Theory of the Torque Converter.*

By E. K. Sandeman, *Ph.D.* (*London*), *B.Sc.*, *A.C.G.I.*†

Although descriptions of the Constantinesco Torque Converter have appeared at different times, and at least one detailed description of its mode of operation has been published, no exact theory has ever appeared showing how the design constants are affected by the engine performance and the variations of load. It is the purpose of this paper to show exactly how these quantities are related. The complexity of the problem, considered from an ordinary dynamic standpoint, is considerably reduced by the application of a simple method of electrical analogy.

Any physically realizable mechanical linkwork, consisting, as it must, of elements possessing mass and rigidity, may often be usefully represented by an equivalent electrical network containing inductance and capacity, for which calculations relating to energy transmission give results valid for the mechanical linkwork. *A priori*, there is no advantage in so doing, but it happens that electrical theory relating to wave-propagation has outstripped mechanics, and it is convenient to make use of the shortened processes available.

Consideration of three elementary examples will suffice to make the general principle clear. In fig. 1 are shown three mechanical arrangements and their equivalent electrical circuits. At A, on the left is represented a cam rotated uniformly by any suitable means, and actuating a tappet

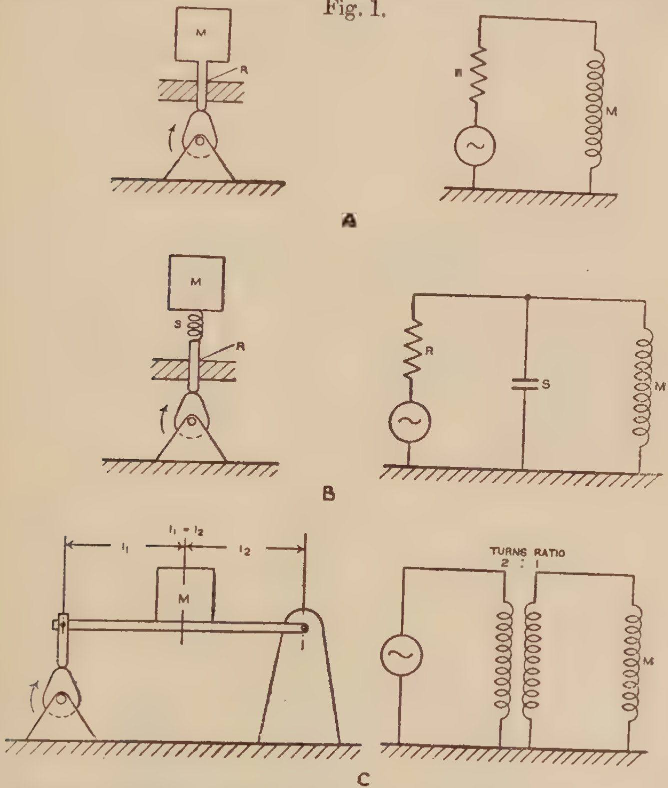
* G. N. Antonoff, Phil. Mag. March 1927.

† Communicated by the Author.

sliding between guides, assumed rigidly connected to the same base or earth as the bearing of the cam-shaft.

The top of the tappet is rigidly connected to a mass M. The rotating cam, in association with the lower end of the tappet, becomes a vibration generator, and, provided that the speed of the cam is never great enough to cause the downward acceleration of the tappet to approach that due

Fig. 1.



to gravity, then the form of the cam specifies the "wave-form" of the generator. The equivalent electrical circuit is shown on the right and requires no explanation. It should be noticed that, whereas mechanically the mass is connected only to the vibration generator, electrically it is connected also to earth. It is not easy to generalize, but there are many times when a mechanical earth connexion, or short circuit, corresponds to an electrical open circuit, and when a mechanical free or open circuit corresponds to an electrical short circuit.

At B is a more complex arrangement in which mechanically a spring is inserted in series between the tappet and the mass. Electrically this becomes a shunt element, since the pressure at the top of the tappet has the alternative of compressing the spring and so charging it with potential energy, or else of accelerating the mass and so giving it kinetic energy. Electrically, when two alternative paths are provided for the flow of energy, they are said to be in parallel.

At C is a vibration generator driving a mass by means of a lever, the mass being situated half-way between the fulcrum and the vibration generator. The lever is here a velocity transformer and also a force transformer in the inverse sense. As viewed from the generator, it reduces the impedance of the mass in the ratio of the square of the pressure ratio.

The most important analogous quantities with which we are concerned in mechanics and electrodynamics are tabulated below, together with the units in which the mechanical quantities are expressed. Three sets of units are here given : the C.G.S. system normally employed, the equivalent Foot Pound Second system, and a system which lends itself rather more readily to practice and which employs the pound instead of the poundal as a unit of force. This is used in this paper for obvious reasons.

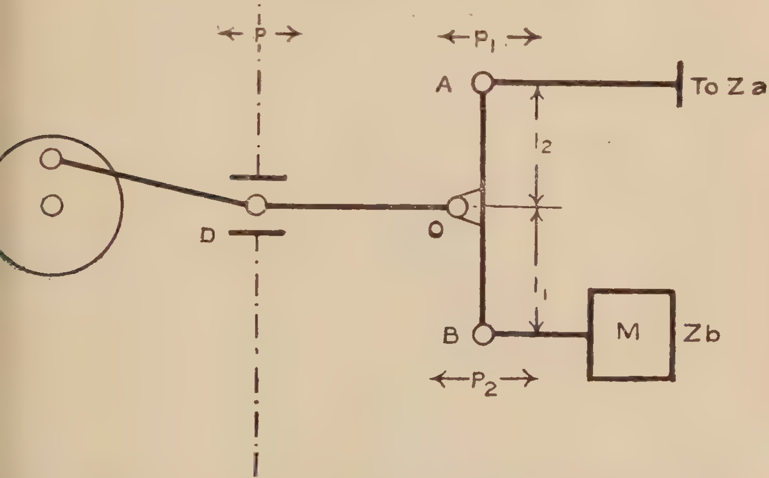
Electrical.	Mechanical.	C.G.S. Units.	F.P.S. Units.	Practical Units.
Electromotive Force.	Vibromotive Force.	Dynes.	Poundals.	Pounds.
Quantity.	Displacement.	Centimetres.	Feet.	Feet.
Current.	Velocity.	Centimetres per second.	Feet per second.	Feet per second.
Resistance or Impedance.	Resistance or Impedance.	Dynes per centimetre per second.	Poundals per foot per second.	Pounds per foot per second.
Inductance.	Inertia.	Grams.	Pounds.	$\frac{1}{g}$ pounds.
Capacity.	Compliance $=\frac{1}{\text{Elasticity}}$.	Centimetres per dyne.	Feet per poundal.	Feet per pound.
$\frac{1}{\text{Capacity}}$.	Elasticity or Stiffness.	Dynes per centimetre.	Poundals per foot.	Pounds per foot.

With these preliminaries the case of the Torque Converter may be considered.

Ideal Theory of the Torque Converter.

The essential construction of this gear is indicated in fig. 2; a driving-point D has a reciprocating motion imparted to it by means of a crank associated with a fly-wheel rotating approximately uniformly. By means of a

Fig. 2.



connecting-rod DO this motion is communicated to any point along the length of a lever AB, the end A of which drives a ratchet supplying energy to the load. The other end B is rigidly fastened to a mass M.

Let P = the R.M.S. force applied to the driving-point in pounds (initially this force may be assumed to be sinuosoidal),

p_a = the resultant R.M.S. force at A in pounds,

p_b = " " " " " B " "

$\dot{x}$ = the velocity of D in feet per second,

$\dot{x}_a$ = " " " A " " " "

$\dot{x}_b$ = " " " B " " " "

Z = the driving-point impedance in pounds per foot per second,

Z_a = the load impedance in pounds per foot per second,

Z_b = the impedance of the mass M in pounds per foot per second,

$O_A = l_2$, $O_B = l_1$.

As a simplification it will be assumed that the lever has no mass and that the load impedance Z_a is a pure resistance. (It will appear later that the equations developed are valid for the case where—owing to the action of the ratchet and the discrepancy between harmonic motion and motion of constant velocity—the load impedance is not a pure mechanical impedance.)

Then

$$p_a = \frac{l_1}{l_1+l_2}\mathrm{P}\,; \qquad p_b = \frac{l_2}{l_1+l_2}\mathrm{P},$$

$$\dot{x}_a = \frac{p_a}{Z_a} \qquad ; \qquad \dot{x}_b = \frac{p_b}{Z_b}.$$

$$\therefore \quad \dot{x}_a = \frac{l_1}{l_1+l_2}\dot{x}_a + \frac{l_2}{l_1+l_2}\dot{x}_b$$

$$= \frac{l_1}{l_1+l_2}\cdot\frac{p_a}{Z_a} + \frac{l_2}{l_1+l_2}\cdot\frac{p_b}{Z_b}$$

$$= \left(\frac{l_1}{l_1+l_2}\right)^2\frac{\mathrm{P}}{Z_a} + \left(\frac{l_2}{l_1+l_2}\right)^2\frac{\mathrm{P}}{Z_b}.$$

$$\therefore \quad Z = \frac{\mathrm{P}}{\dot{x}} = \frac{1}{\left(\frac{l_1}{l_1+l_2}\right)^2\frac{1}{Z_a} + \left(\frac{l_2}{l_1+l_2}\right)^2\frac{1}{Z_b}}. \quad . \quad (1)$$

The above holds for the case where O divides AB internally; it may be shown that, if O divides AB externally, then

$$Z = \frac{1}{\left(\frac{l_1}{l_1-l_2}\right)^2\frac{1}{Z_a} + \left(\frac{l_1}{l_1-l_2}\right)^2\frac{1}{Z_b}} \quad . \quad . \quad . \quad . \quad (1\,a)$$

If $l_1 = l_2$, then

$$Z = \frac{1}{\frac{1}{4Z_a} + \frac{1}{4Z_b}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

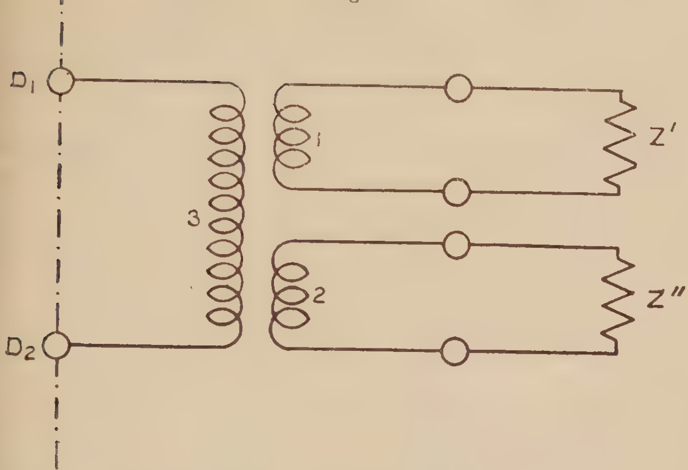
As a check it may be noticed that, if $Z_a = Z_b = X$, then

$$Z = \frac{1}{\frac{1}{4X} + \frac{1}{4X}} = 2X. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Electrical Analogy.

Consider an ideal transformer, having three windings, 1, 2, and 3, operating into loads Z' and Z'', as shown in fig. 3.

Fig. 3.



Let the turns ratio from 3 to 1 be T_1
and „ „ „ „ 3 „ 2 „ T_2,
and let $T_1 + T_2 = 1$,

V = the R.M.S. voltage applied across the driving-points $D_1\ D_2$,
v_1 = the voltage across Z',
v_2 = „ „ „ Z'',
$\dot{i}$ = the current in winding 3,
$\dot{i}_1$ = „ „ „ „ 1,
$\dot{i}_2$ = „ „ „ „ 2,
Z''' = the impedance across the driving-points $D_1\ D_2$.

Then
$$v_1 = \frac{T_1}{T_1+T_2} \cdot V\ ; \qquad v_2 = \frac{T_2}{T_1+T_2} V,$$
$$\dot{i}_1 = \frac{v_1}{Z'} \qquad ; \qquad \dot{i}_2 = \frac{v_2}{Z''},$$
$$\begin{aligned} \dot{i} &= \frac{T_1}{T_1+T_2} \dot{i}_1 + \frac{T_2}{T_1+T_2} \dot{i}_2 \\ &= \frac{T_1}{T_1+T_2} \cdot \frac{v_1}{Z'} + \frac{T_2}{T_1+T_2} \cdot \frac{v_2}{Z_2} \\ &= \left(\frac{T_1}{T_1+T_2}\right)^2 \frac{V}{Z'} + \left(\frac{T_2}{T_1+T_2}\right)^2 \frac{V}{Z''}, \end{aligned}$$
$$Z''' = \frac{V}{\dot{i}} = \frac{1}{\left(\frac{T_1}{T_1+T_2}\right)^2 \cdot \frac{1}{Z'} + \left(\frac{T_2}{T_1+T_2}\right)^2 \frac{1}{Z''}}, \quad . \quad . \quad . \quad (4)$$

which is identically the same form as equation (1).

If $T_1 = T_2$, then (4) simplifies to

$$Z''' = \frac{1}{\frac{1}{4Z'} + \frac{1}{4Z''}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Compare equations (2) and (5) with the well-known relation for impedances in parallel:

$$\frac{1}{R} = \frac{1}{r_1} + \frac{1}{r_2},$$

or

$$R = \frac{1}{\frac{1}{r_1} + \frac{1}{r_2}},$$

Fundamental Principle.

It is therefore apparent that, considering the simplest case, where the driving-point is connected to the middle point of the lever, the first effect of the Constantinesco gear is to multiply the impedance of the load by 4 and to shunt it with an impedance due to the mass which by electrical analogy $= \frac{4M\omega}{g}$ pounds per foot per second, where

M = the mass in pounds,
g = the acceleration of gravity,
$\omega = 2\pi f$, where f = the frequency of reciprocation in cycles per second.

A secondary effect of equal or greater importance, enabling abnormally large starting torques to be obtained, and due to the combined action of the flywheel and the shunt mass, is discussed later.

Velocity Ratio.

The velocity ratio due to the Constantinesco gear is that between the point D and the point A, and is the square root of the resistance ratio between these points. (See Appendix A.)

$$\text{Velocity Ratio} = \sqrt{\frac{\text{Real part of } Z_1}{\text{Real part of } Z}}.$$

The Load Impedance—First Approximation.

The value of Z_1 depends on the load into which the output of the engine operates, and on any gear ratio which occurs

between A and the load. Imagine, for simplicity, that the gear ratio between A and the output is unity, and let

W = the output power of the engine in horse-power,
$550\ W$ = the output power of the engine in foot pounds per second.

Then $Z_1\dot{x}_1^2 = 550\ W$ (since Z_1 is hypothetically a pure resistance).

$$\therefore\ Z_1 = \frac{550\ W}{\dot{x}_1^{\ 2}} \text{ pounds per foot per second.} \quad . \quad (6)$$

(In Appendix B it is shown that if the speed is defined in radians per second angular velocity, then the impedance (resistance) is expressed in pounds feet per radian per second.)

The value of Z is then defined by equation (1). Throughout this discussion the case of an engine driving a road-car is considered, since it is convenient for demonstration purposes, but, provided the load impedance is suitably defined, the explanation holds for any type of load.

Principles of Design.

As is evident from consideration of the conditions at starting, summarized later, the torque converter enables an engine, which only develops appreciable power at high engine speeds, to develop very large torques when operating into large loads. It is evident that in general the smaller the mass the larger will be the engine speed for a given throttle setting, but it is not easy to see what are the determining factors which influence design.

These factors may best be explained by means of two diagrams which will be called the Engine Resistance Diagram (fig. 4) and the Load Resistance Diagram (fig. 5).

The Engine Resistance Diagram.

In Appendix B it is shown that if

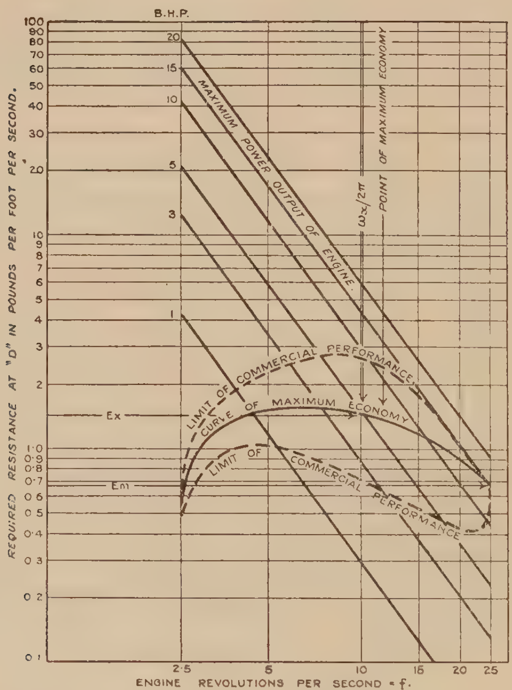
W = the power transmitted along a shaft in horse-power,
f = the speed of the shaft in revolutions per second,
R = the resistance looking into the shaft in pounds feet per radian per second,

then
$$R = \frac{550 W}{4\pi^2 f^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For any fixed power delivered by any engine there are therefore a series of single values of engine speed corresponding to each value of resistance into which the engine

works. On fig. 4 are shown a series of straight lines relating R and f for different values of horse-power. (It is possible to portray these relations by straight lines since logarithmic scales are employed for both R and f.) Although shown for a limited range of powers, these are perfectly general and have no special reference to any one type of engine. They will be referred to as power lines.

Fig. 4.



For any engine there is an optimum speed at which it is capable of delivering a given power, so that for any one engine there is one point on each of the power lines of the engine diagram corresponding to the optimum load. It may be imagined either that this is the most economical speed, or that it is the most efficient speed. The most economical speed may be defined, for a given horse-power, as that speed at which the running cost per hour is a minimum, while the most efficient speed may be defined, for a given horse-power,

as the speed at which the given power is delivered with minimum petrol consumption. The economy basis appears to be of greatest general importance, although there may be cases where the efficiency basis is the most important.

On fig. 4 are plotted a series of hypothetical points, imagined to represent the performance of an individual engine, corresponding to the speeds at which each power (marked on the power line on which the plotted point lies) is supplied with maximum economy. These points are joined together by a heavy line marked "Curve of Maximum Economy." On each side of this line, and running in the same general direction, are two dotted lines representing the locus of the points on each power curve at which the performance of the engine becomes uncommercial. The distance apart of these lines, measured along the power lines and projected on to the axis of engine speed, then becomes a measure of the flexibility of the engine. The area contained between them evidently contains every condition under which it is desirable the engine should operate. The curve of Maximum Economy then gives the relations between the engine speed and the optimum resistance into which the engine should operate. One point on this curve corresponds to the most economical speed and power of the engine.

The Load-Resistance Diagram.

If R is the load resistance in pounds per foot per second as derived in Appendix D, then W being the power in horse-power and $\dot{x}$ the velocity in feet per second, from Appendix B,

$$W = \frac{R\,\dot{x}^2}{550}.$$

$$\therefore \quad R = \frac{550\,W}{\dot{x}^2}. \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

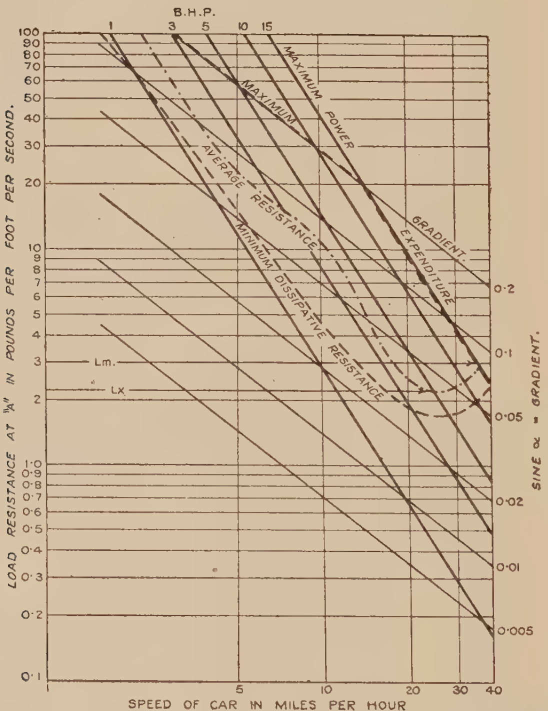
Assuming ρ of Appendix D to be unity for simplicity (*i.e.*, assuming the peripheral velocity of the ratchet = the velocity of the car with regard to the ground-surface) for any fixed value of power delivered to the load, there are a series of single values of resistance at the ratchet-driven rotor. On fig. 5 the heavy lines relate R and $\dot{x}$ for different values of horse-power. These power lines are also perfectly general and have no reference to individual characteristics of apparatus or circumstances.

In Appendix D it is shown that for a given gradient making an angle α with the horizontal the resistance

$$R = \frac{M_c \sin \alpha}{\dot{x}}, \quad \ldots \ldots \quad (10)$$

where M_c is the weight of the car in pounds—that is, R is inversely proportional to the velocity. On fig. 5 the series of light ruled lines relate R and $\dot{x}$ for different values of gradient for the case of a car weighing 2000 lb.

Fig. 5.



The above lines take no account of the opposing forces brought into play by the passage of the car through air and dissipative losses due to bad road surfaces. The dotted line on fig. 5 marked "Minimum Resistance" may be imagined to determine the speed at which a particular car weighing 2000 lb. is impelled along the level by the expenditure of a given horse-power. It may be regarded either as a curve

between horse-power and speed or between dissipative resistance and speed, and it is the latter which is of immediate interest. By adding the ordinates of the minimum resistance curve to the ordinate of each gradient curve, a new set of gradient curves would be obtained, which would show for each gradient the true relation between horse-power and speed, or resistance and speed. This has not been done here as it constitutes an added complication and is not essential to the explanation. It may be noted that to the eye the position of the maximum gradient curve, representing the steepest gradient to be experienced, would be moved very little by the addition of the minimum resistance curve. It is apparent that the performance of the engine is bounded at the top of the diagram by the "Maximum Gradient" curve and the "Maximum Power Expenditure" curve, and at the bottom of the diagram by the "Minimum Resistance" curve. A curve may now be imagined to be drawn across this area, which passes through the points on each power line corresponding to the speeds at which each power is most frequently used. Such a line has been drawn and has been labelled "Average Resistance."

It is evident that an ideal gear inserted between the load and the engine would make any resistance, appearing within the area of performance on fig. 5, appear as a resistance, facing the engine, corresponding to the intersection of the curve of Maximum Economy on fig. 4 and the common power line, *e.g.* Any resistance on fig. 5 lying on the power line 5 B.H.P. would appear at the point D as a resistance of 1·45, corresponding to the intersection of the curve of Maximum Economy and the power line 5 B.H.P. on fig. 4. This not being possible, it is evidently desirable that every resistance lying within the area of performance on fig. 5 should appear within the area of performance on fig. 4 plotted on the common power line, and should fall as near to the curve of Maximum Economy as possible. Since the Torque Converter contains only two variables, the lever ratio $\left(\frac{l_1}{l_1+l_2}\right)$ and the mass M, it is evident that the gear can only be arranged to make two points on the area of performance of fig. 5 lie exactly on the curve of Maximum Economy of fig. 4 when seen through the gear.

It is evidently desirable to exercise considerable care in choosing these two points. It is not desired to follow up all the lines of argument which radiate from this centre, and therefore it will be assumed that the two points on each diagram have been chosen.

On the load diagram has been chosen firstly the point at which the maximum horse-power developed, imagined to be 15 B.H.P., is most frequently used, where the 15 B.H.P. power line cuts the Average Resistance curve. The corresponding resistance is L_m.

The second point is that at which the average B.H.P. (5 B.H.P.) is most frequently used. The corresponding resistance is L_x.

On the engine diagram has been chosen firstly the point at which 15 B.H.P. is delivered with maximum economy; the corresponding resistance is E_m and the corresponding engine speed is ω_m.

The second point is that at which 5 B.H.P. is delivered with maximum economy; the corresponding resistance is E_x and the corresponding engine speed is ω_x.

L_m is to be matched to E_m, and L_x to E_x. The value of the shunt mass and O, the point of connexion along AB (fig. 2) can now be determined directly from L_m, E_m, L_x, E_x, ω_m, and ω_x.

When the load resistance at A (fig. 2) is L_M, the impedance facing the engine at D (or O) must be E_m.

Hence, from equations (1) and (1 *a*)

$$E_m = \frac{1}{\left(\frac{l_1}{l_1 \pm l_2}\right)^2 \frac{1}{L_m} + \left(\frac{l_2}{l_1 \pm l_2}\right)^2 \frac{g}{jM\omega_m}} \quad . \quad . \quad . \quad (11)$$

Similarly,

$$E_x = \frac{1}{\left(\frac{l_1}{l_1 \pm l_2}\right)^2 L_m + \left(\frac{l_2}{l_1 \pm l_2}\right)^2 \frac{g}{jM\omega_m}} \quad . \quad . \quad . \quad (12)$$

Rationalizing equations (11) and (12) and equating reals (the unreals may be neglected in the final count, as these are neutralized in effect by the flywheel), the following equations are obtained:—

$$E_m = \frac{\frac{1}{L_m}\left(\frac{l_1}{l_1 \pm l_2}\right)^2}{\frac{1}{L_m^2}\left(\frac{l_1}{l_1 \pm l_2}\right)^4 + \frac{g^2}{M^2\omega_m^2}\left(\frac{l^2}{l_1 \pm l_2}\right)^4}, \quad . \quad (13)$$

$$E_x = \frac{\frac{1}{L_x^2}\left(\frac{l_1}{l_1 \pm l_2}\right)^2}{\frac{1}{L_x^2}\left(\frac{l_1}{l_1 \pm l_2}\right)^4 + \frac{g^2}{M^2\omega_x^2}\left(\frac{l_2}{l_1 \pm l_2}\right)^4} \quad . \quad . \quad (14)$$

The plus signs are derived if equation (1) is used, and the minus signs if equation (1 *a*) is used.

It should be noted that if AB (fig. 2) is divided internally by O, then

$$\frac{l_2}{l_1+l_2}=1-\frac{l_1}{l_1+l_2}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

If AB is divided externally by O, then

$$\frac{l_2}{l_1-l_2}=\frac{l_1}{l_1-l_2}-1. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

There are thus only two unknowns in equations (13) and (14); that is, M and $\left(\frac{l_1}{l_1-l_2}\right)$. It is evident that the value of l_1+l_2 may be fixed from mechanical considerations other than those with which the above equations are concerned.

The simultaneous solution of equations (13) and (14) gives the value of M and the value of $\frac{l_1}{l_1+l_2}$; that is, the value of $\frac{\text{OB}}{\text{AB}}$ and $\frac{\text{OA}}{\text{AB}}$.

If the solution to these equations gives an impossible value for M, or one which makes the departures from ideal relationships at slow speeds intolerable, then exact resistance matching at the point first chosen mu-t be abandoned and other more suitable points chosen. Alternatively there may be substituted for M a mechanical network whose reactance frequency curve differs from that of a pure mass.

Having chosen suitable values of M and $\frac{\text{OB}}{\text{OA}}$, the performance area of fig. 5, as seen through the gear, may be plotted on fig. 4, and this area should lie within the performance area of fig. 4. This can be done by using equation (13), where L_m and ω_m are considered to refer to any point on the periphery of the area of performance on fig. 5, and E_m is the resulting impedance presented towards the engine.

Conditions at Starting.

Constantinesco, in a recent paper before the Royal Society of Arts, has explained what occurs at starting; but for completeness this operation phase is recapitulated. Initially, the car being at rest, the engine is caused to start rotating, and, like the impedance of an air-gap in the electrical case, the impedance of the load is initially infinite, and remains so until the car moves continuously forward. This happens when the forces on the ratchet are sufficient to overcome the back forces brought into play by the binding together of

mutually rotating parts and the unevenness of the road. All the velocity is therefore initially delivered to the shunt mass, and all the power developed by the engine goes into the flywheel. The shunt mass periodically removes a certain fraction of the energy in the flywheel from it during one quarter cycle, and returns it during the next. As the flywheel accelerates under the influence of the continuously supplied power, the velocity of the shunt mass increases and the exchange of energy between the flywheel and the shunt mass becomes greater, and hence the forces brought into play to effect this exchange become greater. The ratchet becomes the fulcrum for the lever which serves as a link between the shunt mass and the flywheel for the mutual energy exchange, so that the reactive forces increase at a rate nearly directly proportional to the engine torque and inversely proportional to the inertia of the flywheel. This rate of increase is very rapid, since the engine flywheel need be little heavier than in a normal car, and it is a matter of common experience how quickly the engine speeds up when the accelerator is depressed on no load.

As soon as the forces on the ratchet reach a value sufficiently large to overcome the reaction forces experienced at zero speed, the car moves forward and continues to accelerate until a condition of equilibrium is reached represented by resistance matching. Assuming the car has been designed on the principles outlined above, the engine will not be running at its most economical speed unless the throttle is set at a definite position corresponding to the value of load resistance experienced. This, of course, depends on the gradient, the road surface, and the friction in the bearings of the car. It is a simple matter to have an indicator on the car to show whether the throttle is in advance or in retard of the most economical position. The chief value of such an indicator would no doubt be to educate the driver to the feel of the car when running under the optimum conditions.

The Load Impedance—Second Approximation.

The relations discussed above are plainly valid for the case where the load resistance connected to the ratchet is a pure resistance.

It is not easy to represent this in terms of ratchet motion, and no attempt will be made to do so.

The practical case appears quite different, since during part of its travel the ratchet is not in contact with the ratchet-driven rotor, and a further complication is introduced

because the rotor moves with practically constant velocity during the time of contact ; this constancy of velocity is due to the large inertia associated with the rachet-driven rotor, afforded by the mass of the car which is in series with the ratchet-driven rotor. Contact is maintained during a relatively large part of each half cycle, owing to the "give" or compliance (reciprocal elasticity) in the contact. This compliance is in shunt to the rotor resistance, since the v.m.f. in the ratchet may either turn the rotor or charge the compliance with displacement.

Provided the resultant resistance is suitably defined, the relations developed above are also valid for the practical case.

In the practical case the load resistance is defined as the relation between the mean power over a half cycle, and the square of the R.M.S. pressure over a half cycle of the reciprocating motion.

Since the ratchet is double-acting, it may be regarded as a normal impedance containing a number of sources of vibromotive force of frequencies which are multiples of that of the impressed vibromotive force and which form a Fourier series. This is subject to the rider that these v.m.f.'s may be assumed to cause "circulating velocities" which pass mainly through the shunt compliance and the shunt mass and finally cause periodic fluctuations of the engine speed of very small magnitude. No power is dissipated by these circulating velocities. The power necessary to drive these multiple-frequency velocities through the load is derived from the modification of the time-velocity curve of the ratchet (from sinusoidal form), and since they are rectified the power is all usefully expended.

Since the ultimate effect of these multiple frequencies is only a small fluctuation in the speed of the motor (at multiple frequencies), the only velocity of importance at the ratchet is that in phase with the impressed v.m.f., so that the load impedance of interest is a pure resistance.

The power supplied to the ratchet per half period of time T is

$$W=\frac{2}{T}\int_0^{T/2} p_A\,\dot{x}_A\,dt, \quad . \quad . \quad . \quad . \quad (17)$$

where p_A and $\dot{x}_A$ are the instantaneous values of the pressure and velocity at A (fig. 2).

If p_1 is the R.M.S. force at A, and R_A is the unshunted resistance at A, *i. e.* in the absence of a shunt compliance,

$$R_A=\frac{p_1^2}{W}.$$

This is equivalent to saying that R_A is equal to the direct load resistance at the ratchet-driven rotor. This can be seen to be true, since the system is very closely related to an electrical system consisting of a two-pole (commutator) D.C. generator delivering current to a resistance through a very large inductance. The value of effective resistance is unaltered, either by the wave-form or the presence of the series inductance.

The presence of a shunt reactive element, however, does affect the effective resistance. If C is the shunt compliance in feet per pound, then

$$Z_a = \frac{\frac{R_A}{jC\omega}}{R_A + \frac{1}{jC\omega}}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This follows directly from the electrical impedance of a resistance shunted by a condenser. By inserting the value of Z_a so obtained in equation (1) and taking the real part of Z, the resistance into which the engine must operate may be obtained. As explained before, the reactive component of Z may be neglected.

Conclusion.

It has not been attempted to lay down complete principles relating to the basis of design, since these are entirely dependent upon load requirements and the individual characteristics of particular types of prime mover. It is, however, considered that the entire field has been surveyed in sufficient detail to enable the factors affecting design to be weighed and mutually assessed in value, so that a basis for design immediately follows. When this has been established, it is only necessary to apply the ideal theory to arrive at design dimensions.

The author would like to express his very great appreciation of the sympathy given to him, and the suggestions made to him by Mr. R. Appleyard and Mr. A. D. Bloomlein in connexion with the preparation of this paper, to the former of whom its appearance is entirely due. The system of units employed is similar to that used by Mr. A. E. Kennelly and Mr. H. C. Harrison, to the latter of whom the author is indebted for the idea of shunt and series mechanical elements.

Appendix A.

Proof that the velocity ratio between two points in a transmission link-work is equal to the square root of the ratio of the real parts of the impedances at those points, in the absence of dissipation.

Let $Z_1 = A \underline{|\phi}$ be the impedance at one point,

$Z_2 = B \underline{|\psi}$ be the impedance at the other point,

$\dot{x}_1$ and $\dot{x}_2$ being the velocities into Z_1 and Z_2 respectively.

Then, since there is no dissipation, the power passing each point is the same.

$$\therefore \qquad \dot{x}_1^2 A \cos \phi = \dot{x}_2^2 B \cos \psi.$$

$$\therefore \qquad \frac{\dot{x}_1}{\dot{x}_2} = \sqrt{\frac{B \cos \psi}{A \cos \phi}}$$

$$= \sqrt{\frac{\text{Real part of } Z_2}{\text{Real part of } Z_1}}.$$

Appendix B.

Power Transmission by Shafts.

Let τ = the torque on the shaft in pounds feet,

ω = the angular velocity in radians per second,

$\dot{x}$ = the peripheral velocity of a cylinder in the shaft of unit radius, in feet per second,

p = the force in pounds required to produce a torque τ when acting at unit radius.

Then $\dot{x} = \omega$ and $p = \tau$, and the power transmitted $= p\dot{x} = \tau\omega$ foot pounds per second.

The resistance

$$R = \frac{p}{\dot{x}} = \frac{\tau}{\omega} \text{ pounds feet per radian per second.}$$

The above may be expressed in words :—

Since the torque of a force applied at unit radius is numerically equal to the force, and the peripheral velocity of a shaft of unit radius is numerically equal to its angular velocity, the impedance of the (mechanical) circuit in pounds feet per radian per second is numerically equal to its impedance at unit radius in pounds per foot per second.

The power transmitted in horse-power :

$$W=\frac{px}{550}=\frac{\tau\omega}{550}=\frac{R\dot{x}^2}{550}=\frac{R\omega^2}{550}.$$

$$\therefore\ R=\frac{550\ W}{\omega^2}=\frac{550\ W}{4\pi^2 f^2}\ \text{pounds feet per radian per second,}$$

where f is the speed of rotation in revolutions per second.

Appendix C.

Resistance Relations each side of a Crank converting Continuous Rotation into Reciprocating Motion.

The crank is assumed to be of radius r, and the crank-rod to be infinitely long.

ω = the speed of rotation in radians per second $=2\pi$.

f = the frequency of reciprocation,

$\omega r\sin\omega t$ = the instantaneous velocity of the reciprocating end of the connecting-rod,

$\frac{\omega r}{\sqrt{2}}$ = the R.M.S. velocity of reciprocation,

R_D = the resistance on the continuous rotation side in pounds feet per radian per second,

R_R = the impedance on the reciprocating side in pounds per foot per second.

The power on the continuous rotation side = the power on the reciprocating side.

$$\therefore\qquad \omega^2 R_D=\frac{\omega^2 r^2}{2}R_R.$$

$$\therefore\qquad R_D=\frac{r^2}{2}R_R.$$

Appendix D.

Mechanical Resistance of a Mass on a Gradient.

Consider a mass of M pounds on an inclined plane, making an angle α with the horizontal, travelling along the plane under the impetus of a force P at a velocity $\dot{x}$. Let R be the apparent resistance in the absence of friction.

Then $$P=M\sin\alpha.$$

The power supplied to the mass

$$=R\dot{x}^2=P\dot{x}.$$

$$\therefore\qquad R=\frac{P}{\dot{x}}=\frac{M}{\dot{x}}\sin\alpha.$$

If the relative peripheral velocities of the active surface of the ratchet-driven rotor, and the road wheels of a car, assumed to take the place of the mass M above is ρ (greater than unity) where the velocity of the road-wheel periphery is the greater, then the resistance looking into the ratchet-driven rotor

$$=\frac{R}{\rho^2}.$$

Appendix E.

Effect of Change of Load on Engine Speed.

Under any given running conditions, when the load resistance is increased, for instance, by increase of gradient, the engine will sometimes definitely accelerate and sometimes decelerate without the position of the throttle being altered. This is equivalent to saying that increase of load resistance sometimes produces a decrease in the resistance presented towards the engine, and sometimes an increase.

Referring to equation (13), the resistance presented towards the engine,

$$E_m=\frac{\frac{1}{L_m}\left(\frac{l_1}{l_1\pm l_2}\right)^2}{\frac{1}{L_m^2}\left(\frac{l_1}{l_1\pm l_2}\right)^4+\frac{g^2}{M^2\omega_m^2}\left(\frac{l_2}{l_1\pm l_2}\right)^4},$$

where E_m and L_m are now taken to represent respectively general values of resistance presented towards the engine and of load resistance, and ω_m is the corresponding engine speed.

Putting $\left(\frac{l_1}{l_1\pm l_2}\right)^2=A$ and $\left(\frac{l_1}{l_1\pm l_2}\right)^2=B$,

$$E_m=\frac{AL_m\times\frac{M^2\omega_m^2}{g}}{\frac{A^2M^2\omega_m^2}{g}+B^2L_m^2}.$$

When $L_m=0$, $E_m=0$;
and when $L_m=\infty$, $E_m=0$.

Differentiating for a maximum, it may be shown that E_m is a maximum when

$$L_m=\frac{A}{B}\cdot\frac{M\omega_m}{g}.$$

Hence, if L_m is less than this value, and increases in value, the resistance will increase and the engine will slow down. If L_m is greater than this value, and increases, the engine will speed up.

LXXIII. *The Viscosity Factor in Emulsification.*

By R. Christie Smith, *Carnegie Teaching Fellow.*

THE idea that liquids have a surface viscosity differing from that of the interior can be traced back to the writings of Descartes and Rumford. To Plateau ('Statique des Liquides,' vol. ii.), however, is due the development of the idea. He differentiates between two viscosities of a liquid—an internal viscosity determined in the usual manner by a capillary tube, and a superficial viscosity, on the measurement of which very little quantitative work has been done. Plateau measured the superficial viscosity by means of a magnetic needle floating on the surface of the liquid and taking the relative times for it to swing through a certain arc. He showed that liquids and solutions could be divided into three classes. In the first the superficial viscosity was double the internal, *e. g.* water and most aqueous solutions; in the second the superficial viscosity was a fraction of the internal viscosity, *e. g.* alcohol, turpentine, ether; and in the third the superficial was many times greater than the internal, *e.g.* albumen solutions. Further contributions were made to the subject by G. Luvini (Phil. Mag. 1870, xl. p. 190), Tomlinson (Phil. Trans. 1871, clxi. p. 51), Marangoni (*Nuovo Cimento*, 1871–72, v.–vi. p. 260, and subsequent papers).

Oberbeck (*Ann. der Physik*, 1880, xi. p. 634) applied the method of the vibrating rod to the measurement of the superficial viscosity, confirming the results of Plateau. His results were further confirmed by Stables and Wilson (Phil. Mag. 1883, xv. p. 406), working with the apparatus described by Grotian (*Ann. der Physik*, 1876, clvii. p. 237). In 1890, Lord Rayleigh directed his attention to the subject, and set out to find, if possible, the superficial viscosity of a clean surface. His paper (Proc. Roy. Soc. 1890, xlviii. p. 127) contains a description of the method adopted to obtain a clean surface, and he found that as the surface was successively cleaned the superfical viscosity fell in value till equal with the internal, as measured by the time of swing of a needle.

Ramsden (Proc. Roy. Soc. 1923, lxxii. p. 156), working from another standpoint altogether, showed that, quite apart from evaporation, solid or highly viscous coatings are formed more or less rapidly on the free surfaces of all proteid

* Communicated by the Author.

solutions, and that similar coatings of viscous matter are formed at the interface of every pair of liquids examined which, without being of high viscosity, are capable of forming persistent emulsions. He gave a long list of substances which gave intense superficial viscosity, but to date no experimental details have been published.

Hillyer (J. A. C. S. 1903, xxv. p. 513) investigated the interdependence of surface tension, viscosity, and emulsifiability. He came to the conclusion that, while in the case of thick liquids, *e. g.* gum solutions of pharmacists, extreme viscosity was a large factor, it did not, as a rule, mean increased emulsifiability.

Clark and Mann (J. Biol. Chem. 1922, lii. p. 157) made an extensive study of emulsifiability, and came to the conclusion that viscosity was not the predominating factor. Clayton ('Theory of Emulsions and Emulsification,' 1923, p. 41) says: "The conclusion that viscosity aids emulsification solely by virtue of the hindrance offered to coalescence of the dispersed globules, and is not the cause of emulsification, has been accepted by the majority of investigators in this field."

While Plateau has been extensively quoted throughout in publications on emulsions, his differentiatiation between viscosity and superficial viscosity does not appear to have been sufficiently appreciated. While the viscosity as measured by Plateau is that at the air/liquid interface, that of interest in connexion with emulsions is at a liquid/liquid interface, and is therefore appropriately termed the "interfacial viscosity." It therefore appeared that it would be of interest to investigate the relationship between emulsifiability and interfacial viscosity. This has now been done for a variety of substances. In all cases recorded here there are three substances present, viz. disperse phase, dispersion medium, and emulsifying agent. It should perhaps be emphasized at this point that Plateau's third class were all solutions which gave great adsorption at the surface layer, whereas in the cases described by the author the film was not adsorbed out from the solution, but is introduced mechanically from the outside. It allows in this manner the interfacial viscosity of films formed by insoluble substances to be determined.

It had been noted by the author that with kaolin as emulsifying agent and water along with pure benzene, benzol, and liquid paraffin, different emulsifiabilities were obtained. The emulsions obtained with benzol and liquid paraffin were comparable (Table I.), but that with pure benzene was considerably poorer.

Table I.

Disperse phase.	Interfacial tension.	Dispersion factor.	Interfacial viscosity.
Pure benzene	33·6	1·13	0·0034
Benzol	22·6	1·39	0·024
Liquid paraffin	44·6	1·34	0·020

Kaolin present in each case.

From the point of view of interfacial tension, it would have been expected that liquid paraffin would have given the poorest emulsion and benzol the best. So a further factor had to be investigated. It will be seen from the table that benzol and liquid paraffin give comparable interfacial viscosities. The interfacial viscosity was measured by the method of Stables and Wilson (*loc. cit.*). In the preliminary experiments a brass disk was used, and subsequently both nickel and glass disks were used without any appreciable difference in results. These disks were suspended so that the interface of the liquids being investigated was half-way up the side. In all the tables given, the interfacial viscosity is simply the logarithmic decrement observed.

It must be noted that the interfacial viscosity here measured must be considerably greater than that detected by Plateau. For instance, in some preliminary experiments using a brass disk the following values were obtained:—

	Log. dec.
Water just level with bottom of disk	0·015
do. more than half-way up	0·018
do. just above top of disk	0·021
Disk completely immersed	0·032

It will be seen that in this case the viscosity is that due to the surface friction of the disk, and naturally doubled when completely immersed. When a 0·2 solution of saponin was substituted for water the following results were obtained:—

	Log. dec.
Solution just level with foot	0·30
Almost immersed	0·29
Completely immersed	0·0059

N.B.—These figures are not comparable with those obtained for water above, as the moment of inertia had to be considerably increased to obtain a reading at all.

It is therefore evident that when the disk is swinging in the surface a very appreciable viscosity is manifest. It is not, therefore, in the case of liquids which would be classed under Plateau's first group but those under the third group which will give a viscosity measurable by this method and favourable to emulsification.

The results obtained are set out in Table II. Paraffin and xylene give the best correspondence. Powders which do not form emulsions have been found to give a very slight increase in viscosity. Most of the powders chosen have been selected from the lists given by Hofmann (*Z. phys. chem.* 1913, lxxxiii. p. 385) and Reinders (*Z. koll. chem.* 1913, xiii. p. 235) as being those which tended to collect at the interface. It is to be noted, however, that some of the best emulsions have been formed by kaolin which is stated to be preferentially wet by water. In one or two cases solids were found which gave evidence of emulsifying but showed no appreciable interfacial viscosity. Copper sulphide and lead carbonate were outstanding examples of this. On the other hand, aluminium hydroxide and lead chloride gave a high interfacial viscosity but comparatively small emulsification.

The term "emulsifiability" is used throughout this paper as embracing two definite ideas. The first is the ease with which the disperse phase is dispersed, and the second is the stability of the resulting dispersion. A good emulsifying agent must possess both these properties; hence emulsifiability must include both these factors. How they have been combined into one numerical factor is explained under "Experimental."

Experimental.

The apparatus used was very similar to that described by Grotian (*loc. cit.*). A wire about 1·25 m. long supported the cradle C and the disk D. The suspension had two swivels A and B at right angles to each other, and rigid as regards rotatory movements so as to ensure that the disk can hang horizontal. In the cradle C iron rods of different weight may be placed in order to alter the moment of inertia of the system. The moment of inertia of the system was determined by the usual method and found to be 535·2 cgs. units. In some of the preliminary experiments a small disk of 2·8 cm. diameter was used, and also a cylinder 2·8 cm. in diameter and 2·0 cm. in length. For most of the determinations, however, a disk of nickel 7 cm. in diameter and 2 mm. thick was used. The cradle C carried a dumb-bell weighing

TABLE II.

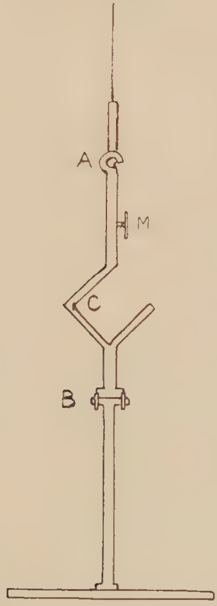
Agent.	Benzene.		Toluene.		Xylene.		Liquid Paraffin.		Petroleum Ether.		Carbon Tetrachloride.	
	D.F.	I.V.	D.F.	I.V.	D.F.	I.V.	D.F.	I.V.	D.F.	I.V.	D.F.	I.V.
Kaolin	1·13	·032	1·11	·038	1·30	·10	1·34	·20	1·38	·22	1·14	·0052
Aluminium hydroxide	1·00	·019	1·00	·012	1·00	·019	1·00	·06	1·00	·036	1·00	·015
Magnesium hydroxide	1·11	·0052	1·20	·0077	1·25	·13	1·33	·096	1·37	·0083	1·03	·010
Fullers' earth	1 07	·0036	1·10	No film.	1·17	No film.	1·05	·029	1·34	·0043	1·06	·0017
Kieselguhr	1·11	·0044	1·06	·0015	1·18	·006	1·00	·054	1·00	·0049	1·11	·0024
Silica	1·00	·0054	1·00	·0010	1·00	·0011	1·00	·010	1·15	·0067	1·00	·0033
Barium sulphate	1·05	·0013	1·00	No film.	1·00	No film.	1·14	·025	1·12	·0013	1·03	·0071
Magnesium oxide	1·00	No film.	1·00	No film.	1·00	No film.	1·05	·006	1·00	No film.	1·04	No film.
Lead chromate	1·16	·024	1·24	·062	1·31	·13	1·26	·022	1·09	·04	—	—
Zinc sulphide	1·03	·0016	1·07	·0014	1·13	·010	1·06	·011	1·06	·0018	—	—
Copper sulphide	1·21	·002	1·15	·0024	1·31	·004	1·41	·017	1·13	·0023	—	—
Barium carbonate	1·12	·007	1·09	·013	1·10	·04	1·00	·110	1·09	·013	—	—
Zinc oxide	1·52	·45	1·42	·50	1·52	·25	1·69	·92	1·49	·40	—	—
Zinc carbonate	1·13	·0045	1·11	·002	1·11	·003	1·30	·019	1·12	·004	—	—
Lead chloride	1·00	·005	1·00	·003	1·00	·003	1·00	No film.	1·00	No film.	—	—
Lead carbonate	1·14	·50	1·14	·85	1·24	·70	1·34	·34	1·21	·50	—	—

D.F. = Dispersion factor.

I.V. = Interfacial viscosity = Logarithmic decrement.
I.V. for Water/Benzene = ·0010.
I.V. for Water/Liquid paraffin = ·0053.

1489 gm. and with a moment of inertia of 52,278 cgs. units. The period of the system was 13·9 sec. A small mirror mounted at M reflected the light from a lamp on to a scale at a distance of about 2 m. The disk was suspended in an oblong photographic dish to prevent rotation of the interfacial film along the disk, as tends to happen with a circular dish. The whole apparatus was enclosed in a box open only at one side in order to exclude draughts.

Fig. 1.



In order to make a determination, water was poured into the photographic dish until the level of its surface was halfway up the suspended disk. Benzene (or other liquid) was then poured in to cover the disk completely. The emulsifying agent (1 gm.) was then carefully sprinkled over the whole surface by means of a piece of muslin. The powder had been previously passed through a sieve of 120 mesh. The solid fell through the benzene and formed a film at the interface. It was found that by leaving the film for 20 to 30 minutes more consistent (and in some cases higher) readings were obtained. No improvement in emulsification could, however, be obtained by allowing the powder to remain at the interface before emulsifying. The results were usually reproducible within 10 per cent. and in many cases 5 per cent., even with different experimenters. Readings were

obtained by setting the disk oscillating horizontally by means of a magnet acting on the iron rod in the cradle. The logarithmic decrement was observed as the magnitude of the swing fell from approximately 24° to 12°. In some cases it was impossible to obtain satisfactory readings by means of the large disk (7 cm.) owing to magnitude of the logarithmic decrement, and it was found necessary to make observations with a smaller disk (2 cm.). The smaller disk gave readings approximately one-tenth of the large disk. All the readings given in Table II. have been corrected to the basis of the large disk.

The test emulsions were made by means of the apparatus described fully elsewhere (*Rev. Gen. Coll.* 1927, v. p. 412). Briefly, a cylindrical tube with a hole in it, fitted to a shaft, has soldered to its lower end a disk of brass to which on the under side are attached vanes covered with copper gauze. On rotating, liquid is drawn through the hole in the shaft and thrown out through the gauze. The whole fits in a boiling-tube and emulsifies conveniently a volume of 40 c.c. Equal quantities (20 c.c.) of water and "oil" were placed along with 0·64 gm. solid (=2 per cent.) in the boiling-tube and emulsified for two minutes with the machine rotating 2000 times per minute. The resulting emulsion was then transferred to a flat-bottomed test-tube and allowed to stand for an hour. If unity represents the volume of the "oil" before emulsification, the "emulsifiability" is taken as the total volume of undispersed "oil" and emulsion after emulsification. This will be greater than 1 and less than 2. The numerical value is seen also to depend on two factors—viz. the amount of the oil dispersed, and the dispersity of the emulsion, and will vary directly with them. It therefore gives a simple numerical method of comparing emulsions. For fuller discussion see paper above mentioned.

Summary.

1. Attention is drawn to the fact that Plateau investigated the phenomenon of surface viscosity.

2. Many experimenters have referred to Plateau's work, but have considered chiefly the viscosity of the dispersion medium.

3. The viscosity of the interfacial film, especially that produced when a solid is introduced into the interface, has now been investigated.

4. It is shown that solids giving good emulsifiability give, as a rule, high interfacial tensions.

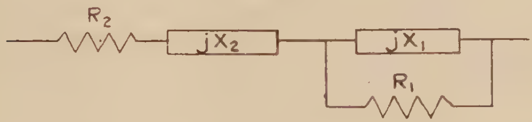
Physical Chemistry Department,
University of Glasgow.

LXXIV. *The Design of Networks for Balancing Telephone Lines.* *By* L. C. Pocock, *M.Sc.**

THE development of telephone repeaters has brought into prominence a circuit design problem that rarely presented itself before—the problem of building a two-terminal network to have a given impedance frequency characteristic. There are several ways of determining the network, but comparatively little has been published on the subject; it is the object of this article to describe a quick and easy way of designing a simple network used in a very large number of cases.

The type of network under consideration (fig. 1) is that

Fig. 1.



in which two resistances are in series, and one of them is shunted by a reactance; in addition a reactance may be required either in series with the line or with the network. The impedance of such a network may be represented by

$$Z = \frac{R_1R_2 + jX_1(R_1+R_2)}{R_1+jX_1} \pm jX_2, \quad . \quad . \quad . \quad (1)$$

where X_1 and X_2 are reactances with proper signs according to their inductive or capacitive nature, and a positive sign before jX_2 means that X_2 is to be in series with the network, while a negative sign means it is to be added in series with the line.

If the impedance of the first member on the right of (1) is denoted by Z_a and plotted in the complex plane for various values of the angular frequency ω, it can be shown that the locus will be the circle having its centre at $R_2 + R_1/2$, and radius $R_1/2$. The second term in (1) represents displacements parallel to the j axis of each point on the circular locus, the amount of the displacement being proportional directly or inversely to ω according as X_2 is inductive or capacitive, and the direction being upwards or downwards according as the sign is positive or negative.

* Communicated by the Author.

The first step in designing a balancing network to have a given frequency characteristic is to plot the given values of Z in the complex plane, marking the values of ω at a number of points; if, then, it is possible to draw a circle centred on the real axis, through the plots, X_2 is zero. (Subject to the fulfilment of a projection condition to be stated later.) In the general case the plots are not circular, and it can be seen from the shape of the locus whether an inductive or capacitive impedance is required to make the locus circular; accordingly three or more suitable points on the locus are chosen, and evenly-divided vertical scales are drawn through each, the divisions of each scale being proportional (directly or inversely) to the value of ω at the point; a circle is then found by trial such that it passes through the same numbered division of each vertical scale, and has its centre on the real axis. The value of X_2 and the corresponding inductance or capacity is readily found from the vertical scales intercepted between the circle and the Z locus; R_1 and R_2 are found from the position of the centre and the value of the radius of the circle, so that X_1 alone remains unknown.

It is a property of circle diagrams * such as the one under consideration that the frequency variable is distributed round the circle in the manner given by setting up a uniform frequency scale parallel to the j axis and projecting the scale on to the circle, from the point on the circle corresponding to infinite frequency as pole; it is desirable to verify that the known frequencies round the circle project in this manner into a linear scale perpendicular to the real axis; when this has been verified, X_1 may be found from the expression,

$$X_1 = \frac{R_1 \sqrt{|Z_a^2| - R_2^2}}{\sqrt{(R_1+R_2)^2 - |Z_a^2|}}, \quad . \quad . \quad . \quad . \quad (2)$$

where X_1 and $|Z_a|$ are corresponding values at any chosen frequency. The same value of inductance or capacity should be derived from X_1 whatever value of the frequency is used in selecting $|Z_a|$, but no checking of the result except as a precaution against arithmetical error is necessary, provided the circle passes accurately through the prescribed points and the frequency scale projects accurately into a truly linear scale; in the event of slight departures from this criterion, X_1 may be calculated for three or four points and an average value found for the reactive element.

* Th. Kopczynski, *Siemens Zeitschrift*, Feb. 1925, p. 75.

Proof.

To prove the expression used in determining X_1, we shall use the notation of elliptic functions * ; but it is the relations between these functions rather than their values as functions of the argument that are made use of, so that they do not appear in the final expression ; for simplicity, equation (2) is proved for the case where X_1 is a capacity reactance ; in the case of inductance the proof is similar.

From (1) we write more explicitly

$$Z_a = \frac{R_1 + R_2 + jR_1R_2C_1\omega}{1 + jR_1C_1\omega}, \quad . \quad . \quad . \quad . \quad (3)$$

whence

$$|Z_a| = (R_1 + R_2)\left[\frac{1 + \dfrac{R_1^2R_2^2C_1^2}{(R_1+R_2)^2}\omega^2}{1 + R_1^2C_1^2\omega^2}\right]^{1/2}, \quad . \quad . \quad (4)$$

which may be rationalized in elliptic functions by the substitutions †

$$sc\, u = R_1C_1\omega, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$k = \left\{1 - \frac{R_2^2}{(R_1+R_2)^2}\right\}^{1/2}; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

then

$$|Z| = (R_1 + R_2)\, dn\, u\,. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now it is readily shown that

$$sc\, u = \left[\frac{1 - dn^2u}{k^2 - 1 + dn^2u}\right]^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Substituting from (6), (7), and (8) in (5) in such a manner as to clear of elliptic functions, we get

$$1/C_1\omega = R_1\left[\frac{|Z_a^2| - R_2^2}{(R_1+R_2)^2 - |Z_a^2|}\right]^{1/2}, \quad . \quad . \quad . \quad (9)$$

which is equation (2) written explicitly for X_1 as a capacity reactance.

If a considerable number of cases are to be worked out,

* The elliptic functions are $sn\, u$, $cn\, u$, $dn\, u$ ($sc\, u$ is used for $sn\, u/cn\, u$) with an implied parameter (the modulus) k. The relations between these functions are those existing between the trigonometric equivalents $sn\, u = \sin\theta$, $cn\, u = \cos\theta$, $dn\, u = \sqrt{1 - k^2\sin^2\theta}$. The elliptic function notation is simpler than the trigonometric, and is more appropriate because the circle diagram used is a simple case of Jacobi's construction. (Dixon, 'Elliptic Functions,' Chap. x. pars. 105 & 107.)

† Dixon, *loc. cit.* par. 89.

tables or curves of the elliptic functions, or their trigonometric equivalents, enable C_1 to be found very easily from (5) and (7) with hardly any numerical calculation at all.

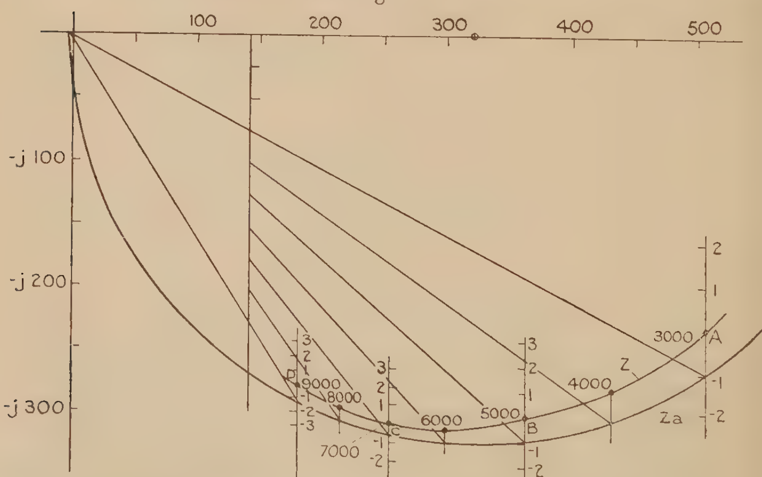
Example.

As an example of this method of designing balancing networks, we shall take an example worked out by Messrs. Robinson and Chamney in illustration of a method developed by them *.

$2\pi f$.	Impedance given.	Calculated network impedance.
3000	$509-j231$	$507-j235$
4000	$432-j281$	$434-j281$
5000	$361-j303$	$366-j303$
6000	$300-j313$	$307-j309$
7000	$254-j309$	$257-j306$
8000	$216-j296$	$217-j297$
9000	$182-j279$	$184-j285$

The required impedance characteristics are shown in the table, and are plotted in the complex plane in fig. 2. The

Fig. 2.



* Inst. P.O. Elect. Engrs., printed paper No. 76, Appendix III. The method adopted is to calculate the slope of the resistance curve at a number of points and plot it against frequency for comparison with standard curves having various values of constant product C_1R_1. C_2 and R_2 are then found by calculating the impedance of the shunted condenser and subtracting from the components of the given impedance characteristic. (See also Dechange, *Bul. Soc. Belge des Électriciens*, Aug. 1924.)

plots are not quite circular, and points A B C D are selected for the vertical scales; a few trials show that a capacity reactance is required for X_1, and accordingly vertical scales are drawn through A, B, C, and D, and marked with arbitrary divisions proportional to $1/\omega$ in each case.

It is easily found by trial that a circle can be drawn almost exactly through the scale-divisions numbered $y=+1$ with centre at $x=290$, or a circle can be drawn through the points $y=-1$ with centre at $x=321$. On applying the test of projecting the points on the circle on to a linear scale, the circle through the points $y=-1$ is found to be the better fit and is therefore adopted. The circle centred at $x=321$ cuts the real axis at -5, so that its radius is 326, and therefore $R_1=652^{\omega}$. R_2 is -5; that is, 5^{ω} added to the line. Measuring the intercept between the Z plot and the circle at $\omega=5000$ we find it to give $X_2=+j20$, whence $C_2=10$ mf. added in series with the line. Finally, calculating X_1 for the value $\omega=5000$, we measure the distance from the origin to the 5000 point on the circle giving $|Z_a|=489$, and evaluating equation (9), we find $X_1=749$ or $C_1=0{\cdot}267$ mf.

For comparison with the characteristic to be matched, the network impedance has been calculated giving R_2 and C_2 their negative signs. The values are tabulated in the table with the measured line impedances. Owing to graphical inaccuracies arising out of the small-scale drawing, the calculated resistance values are a trifle high, and though the balance is quite good, it can be improved by subtracting 2^{ω} from the network impedance; that is, changing R_2 from -5 to -7.

LXXV. *On the Dilution Law for Strong Electrolytes.* *By* R. T. Lattey *.

An examination of the data for the conductivity of strong electrolytes showed empirically that the following formula has a wide range of application:

$$\lambda_0-\lambda=A/(B+V^{\frac{1}{2}}), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A and B are constants peculiar to the solution in question.

This is obviously in accord with Debye and Hückel's [(1)] thesis that at great dilutions $\lambda_0-\lambda$ varies inversely as $V^{\frac{1}{2}}$, and therefore the constant A should be equal to Debye's

* Commuicated by the Author.

$\alpha\sqrt{2}$. It is of interest to compare the new formula with some which have been proposed on other grounds; of these, the most general is the form of Storch's equation which has been recently so freely exploited by Vogel and Ferguson [2]:

$$\lambda_0 - \lambda = K/V^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n is usually between 0·4 and 0·8.

There is also the form used by Debye and Hückel and by Onsager [3], viz.:

$$\lambda_0 - \lambda = A/V^{\frac{1}{2}} - AB/V, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to which the new form must approximate when V is large.

In Table I., Kohlrausch and Maltby's data for KCl (as quoted in Landolt and Börnstein's tables) are compared with values calculated by the three methods referred to, using the constants,

for (1) $\lambda_0 = 130{\cdot}01$, $A = 89{\cdot}47$, and $B = 1{\cdot}82$.

(2) $\lambda_0 = 130{\cdot}04$, $K = 61{\cdot}26$, and $n = 0{\cdot}4520$.

(3) $\lambda_0 = 130{\cdot}01$, $A = 89{\cdot}47$, and $AB = 134$.

TABLE I.

V.	(1).	(2).	(3).	K and M.
10000	129·13	129·09	129·16	129·07
5000	128·775	128·725	128·80	128·77
2000	128·09	128·085	128·105	128·11
1000	127·335	127·34	127·345	127·34
500	126·31	126·31	126·31	126·31
200	124·405	124·505	124·395	124·41
100	122·44	122·395	122·43	122·43
50	119·95	119·49	120·07	119·96
20	115·79	114·37	115·40	115·75
10	112·07	109·40	115·14	112·03
5	107·95	100·17	116·84	107·96
2	102·34	85·67	134·27	102·41
1	98·28	68·78	174·57	98·27
0·5	94·60	45·45	271·54	92·60

It will be seen that whereas the new formula gives agreement within less than 1/10 per cent. up to normal solutions, the others break down when V is between 20 and 50.

The new formula has been tested on a variety of data for uni-univalent salts, both in aqueous and other solutions, and has been found satisfactory over far wider ranges than any other formula with which the author is acquainted.

It is proposed here only to discuss uni-univalent salts in

water at 18° C.; for these the formula is satisfactory in every case examined up to 0·1 N solutions, and in some cases up to greater concentrations.

The data used are those of Kohlrausch, and the results are shown in Table II.

TABLE II.

Salt.	λ_0 found.	λ_0 calcd.	A found.	A calcd.	B.
KBr	132·13	...	92·78	...	2·00
KI	130·69	...	86·69	...	2·00
KCl...........	130·01	130·01	89·47	89·37	1·82
KNO_3	126·44	126·43	90·82	90·45	1·015
KSCN	121·24	...	87·46	...	2·00
$KClO_3$.........	119·60	119·485	88·28	88·18	1·177
$AgNO_3$	115·88	...	88·41	...	0·940
†$KBrO_3$	112·67	112·73	92·58	92·84	1·607
KF	111·34	111·23	81·08	81·70	1·484
NaCl	108·91	108·91	80·55	80·76	1·605
$NaNO_3$	105·32	105·33	81·46	81·84	1·345
LiCl	98·90	98·855	78·90	76·92	1·705
KIO_3	98·48	98·495	80·70	80·84	1·127
*$NaClO_3$	98·17	98·385	79·47	79·57	1·423
$LiNO_3$.........	95·23	93·275	78·10	78·00	1·786
*$NaBrO_3$	91·70	91·63	84·19	84·23	1·735
NaF	90·08	90·13	73·17	73·09	1·334
$NaIO_3$.........	77·40	77·395	72·37	72·23	1·109
$LiIO_3$	67·38	67·34	68·28	68·39	1·138
TlCl	131·33	131·33	91·52 ?	93·82	−2·08
$TlNO_3$	127·75	127·75	97·20 ?	94·90	0·4635
HCl	380·56	381·2	109·1 ?	108·35	0·582
HNO_3.........	378·34	377·6	108·7 ?	109·45	0·592

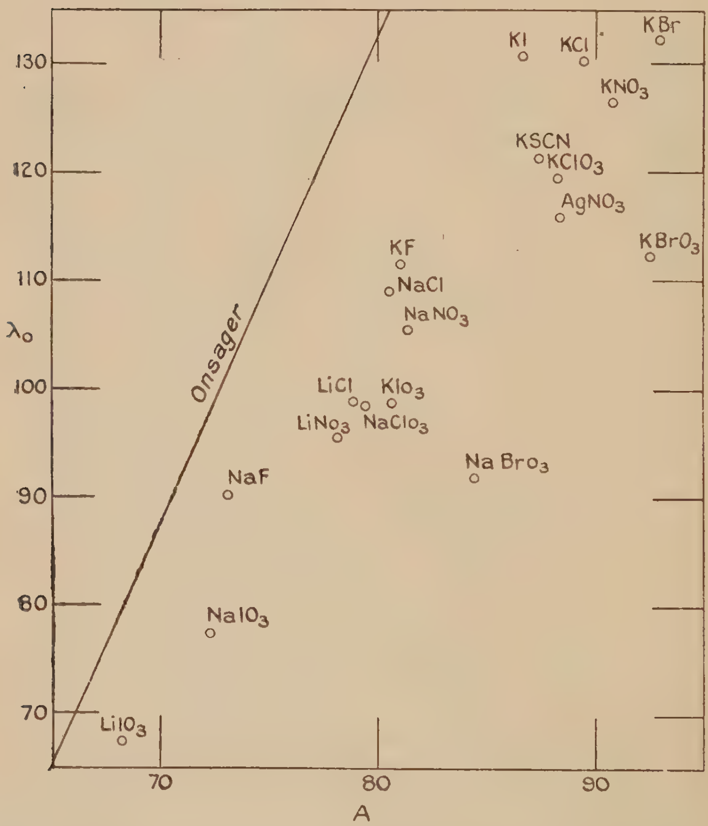
* From data by Flügel, *Zt. Phys. Chem.* lxxix. p. 586.
† " " " Hunt, Journ. Amer. C.S. xxxi. p. 801.

Now, according to Debye and Hückel [1], the A can be expressed by $K_1+K_2\lambda_0 b$, where K_1 and K_2 are factors depending only on the solvent, while $b=\frac{l_1}{l_2}+\frac{l_2}{l_1}$, where l_1 and l_2 are the mobilities of the ions of the salt in question. Redlich [4] has proposed changes in the numerical value of K_2, while Onsager [3] has propounded a theory by which b is replaced by a factor independent of the salt.

If Debye and Hückel are right, then A should be a linear function of $\lambda_0 b$, while if Onsager is right, A should be a linear function of λ_0. Figs. 1 and 2 show that neither of these views is supported by the facts. The values of A

are, however, apparently additive: *i. e.*, we can put $A = a_1 + a_2$ where a_1 and a_2 are characteristic of the anion and kation respectively*. In order to assign a series of such values to the ions, it is necessary first to assign an arbitrary value to one ion, and the rest can then be found by subtraction. In fig. 1 it will be seen that the three simple

Fig. 1.



salts KCl, NaCl, and NaF lie approximately on a straight line, and it has therefore been assumed that there is a linear relationship between a and l for the ions K, Na, Cl, and F. The figures so obtained are shown in Table III., and were used in calculating the column headed "A calc." in Table II.

* At any rate so far as aqueous solutions at 18° C. are concerned.

Fig. 2.

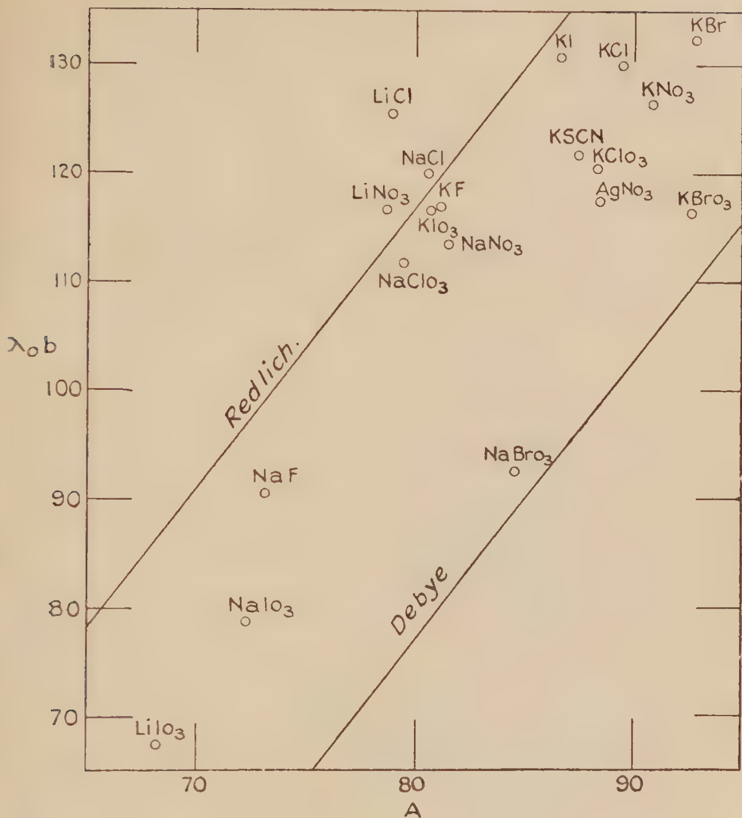


TABLE III.

Ion.	*l.*	*a.*	Ion.	*l.*	*a.*
Cl	66·405	45·26	Li	32·45	31·66
NO_3	62·825	46·34	Tl	64·925	48·56
ClO_3	55·88	44·07	H	314·8	63·1
F	47·625	37·59			
IO_3.........	34·89	36·73	Br	68·53	48·67
BrO_3	49·13	48·73	I	67·09	42·58
K	63·605	44·11	SCN	57·64	43·35
Na	42·505	35·50	Ag	53·06	42·07

Values below the horizontal line depend on a single determination and must be regarded as provisional.

The factor B can, for the present, only be regarded in the nature of a correction term; the value assigned to it is largely affected by small errors in experimental data. A larger mass of data will have to be examined before any generalizations can be attempted.

List of References.

(1) Debye & Hückel, *Phys. Zeit.* xxiv. pp. 187, 305 (1923): Trans. Faraday Soc. 1927.
(2) Vogel & Ferguson, Phil. Mag. l. p. 971 (1925); iv. pp. 1, 232, 300 (1927); Trans. Faraday Soc. xxiii. p. 404 (1927).
(3) Onsager, Trans. Faraday Soc. xxiii. p. 341 (1927); *Phys. Zeit.* xxvii. p. 388 (1926).
(4) Redlich, *Phys. Zeit.* xxvi. p. 99 (1925).

LXXVI. *A Concentrated Arc Mercury Lamp.* By E. L. Harrington, *Ph D., Professor of Physics, University of Saskatchewan, Saskatoon, Sask., Canada* *.

[Plate XVIII.]

ABOUT four years ago a description † was given of a mercury arc lamp in which the arc was confined wholly to a capillary tube. Suggestions as to operation were made, and some advantages discussed. Certain decided improvements in the lamp itself, extensions in its use and additional observations of its characteristics growing out of its increased use in the laboratory suggest this further discussion.

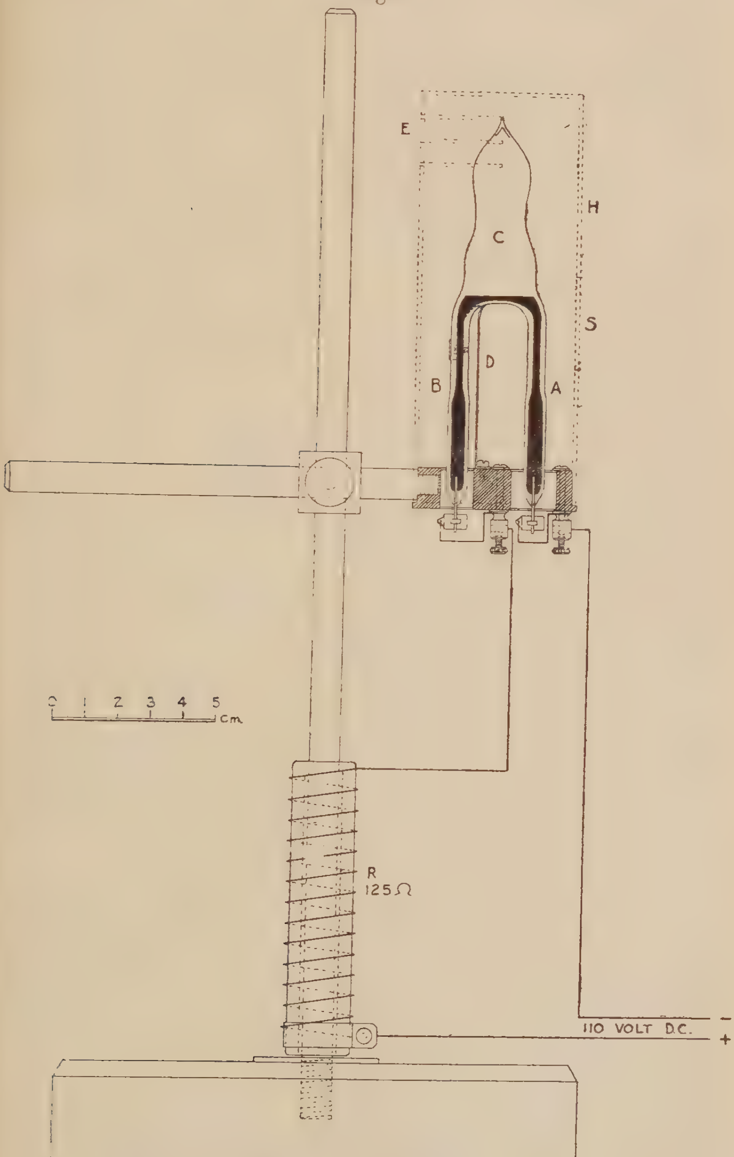
No material changes in dimensions have been made, but the new form, shown in fig. 1, has decided advantages. Its symmetrical form better adapts it for compact mounting in a housing. In this lamp the two legs are exactly alike in construction, being made of pyrex capillary tubing of about 1·5 mm. in bore, and having the lower portions considerably enlarged as shown. The lead-in wires are of tungsten. It has been generally found by those who have used mercury arcs confined either to capillary tubes or to large tubes that the inner tube surfaces become with continued use somewhat less transparent, particularly to the ultraviolet. This effect is especially noticeable in cases where the lamps have been repeatedly overloaded, or where an excess current has been carried for a considerable period. Apparently slight impurities in the mercury accentuate this tendency. With the present lamp having the two legs alike it is possible to interchange the positions of the two legs when one has

* Communicated by the Author.

† Harrington, J. O. S. A. and R. S. I. vol. vii. p. 689, Sept. 1923.

become discoloured, thereby virtually doubling the life of the lamp. A further advantage of the same sort may be

Fig. 1.



obtained by giving the lamp three or even four legs, if desired.

The housing, H, for the lamp is made of thin brass tubing and is provided with a vertical slit, S, directly in front of the arc capillary and cross slits, E, for ventilation at the top as shown. Such a housing makes the lamp suitable for dark-room use and also protects the eyes of the observers. The lamp is supported by one leg by means of a brass clamp D, the latter being mounted on the fibre base. Connexions to the lamp are made by spring clips which are connected to the fixed binding-posts.

For a 120 volt D.C. circuit a series resistance of about 125 ohms and having a carrying capacity of 1 ampere is required. The commercial porcelain tube vitreous enamel-covered resistance units are found highly satisfactory. While the lamp may be operated on any D.C. voltage definitely greater than the lamp voltage (roughly 30 volts, though varying widely with conditions and load) providing the control resistance is properly adjusted, it is best to have a considerable margin to secure definite control. The current required depends upon the size of the capillary tube, but is about 0·7 ampere for the lamp described above.

Preliminary to starting the discharge it must be made certain that the current is actually passing through the lamp and in the direction indicated in fig. 1. With the cover removed, a bunsen flame is applied at the point indicated by A in fig. 1, until the mercury column is broken up and the arc started. If owing to interruption of the service or to other cause the arc should go out, it is exceedingly important to make sure that the mercury column is complete and the current flows before again applying the flame, since dangerous pressures might be developed by a continued application of the flame. Vincent and Biggs * have described an electric heater consisting of a resistance wire applied to the capillary. Such an arrangement should make for convenience, but it increases the complexity of the outfit considerably.

It is possible to construct a lamp suitable for A.C. sources by using the mercury arc rectifier type of construction, but the considerable accessory equipment in the way of transformers of special nature required makes it of doubtful general interest, though a commercial company might render a real service to the laboratories by developing and placing on the market a suitable A.C. outfit.

Compared with the commercial diffuse arc mercury lamp, the lamp described above has for laboratory use the very definite advantages of greater convenience, lower initial cost, and lower current consumption. An even more important

* Vincent and Biggs, Jr. Sc. Instr. vol. i. p. 242, May 1924.

advantage lies in the greater richness of the spectra obtainable, as will be shown by the accompanying Plate. The spectrograms are submitted without detailed analysis in view of the rather voluminous literature on the mercury arc spectra already obtainable.

Pl. XVIII. shows the spectra obtainable from the mercury arc under a variety of conditions, using a Hilger Quartz Spectrograph. Type E–3, Size C. Pl. XVIII. (*a*) was obtained from a Cooper-Hewitt lamp, DP type. The tube of this lamp is of M form, has a total length of about 130 cm., and an external diameter of 2·5 cm. For this spectrogram the current was 4·4 amperes, the tube voltage drop 66 volts, and the time of exposure 30 seconds. The lamp markings indicate that the lamp was designed for 110 volt service and to carry 3·5 amperes. As this spectrogram contains as many lines as are obtainable on say a 2 minute exposure and differs merely in the intensities of the lines shown, it may be taken as typical of the spectra obtainable from a non-concentrated mercury arc discharge in glass.

Pl. XVIII. (*b*) and (*c*) were obtained from a pyrex lamp of the type shown in fig. 1. and having a capillary of 1·58 mm. bore. (*b*) resulted from a 30 second exposure at 26 volts and 0·5 ampere, and (*c*) from the same exposure but with a 28 volt drop and a current of 1·0 ampere. Here again only the difference in the intensities of the lines are in evidence, so either (*b*) or (*c*) may be taken as representative of the spectra obtainable from lamps of this type, when constructed of pyrex glass. A comparison of these with (*a*) shows that the concentrated arc gives about three times as many lines and much greater intensity than is obtainable from a diffuse arc. It may be observed, also, that the spectra extend further into the ultraviolet, though this may be due principally to the use of pyrex glass which has a somewhat lower transmission limit than ordinary glass *. There appears in these, as well as in the following spectrograms, a faint continuous spectrum background, due to the high temperature of operation.

Pl. XVIII. (*d*) and (*e*) were obtained from a lamp of exactly the same design as shown in fig. 1 but constructed of quartz tubing, the capillaries having a 1·32 mm. bore. In (*d*) the current was 0·48 ampere, the tube voltage 29·0 and the length of exposure 80 sec. (*e*) was taken with the same lamp and period of exposure, but with a current of 0·98 ampere and a tube voltage of 39. Just as in the above cases, it

* See Luckiesh, 'Ultraviolet Radiation,' p. 82 or 'Science,' p. 281, Sept. 17, 1926.

appears that the increase in the current affects the intensities but not the number of lines appearing. One advantage of using the quartz is apparent in the large increase in the number of lines obtainable, due to the additional extension into the ultraviolet region. There are twice as many as appear in the spectra obtained from a pyrex lamp of the same construction, and about six times as many as are given by a non-concentrated arc in ordinary glass tubing. The spectra of the quartz and of the pyrex lamps appear to be identical in the visible and the near ultraviolet regions.

Another advantage lies in the possibility of operating the lamp at much higher intensities. This is of particular value in making studies in the ultraviolet region, for it has been found that the ultraviolet intensity increases with increasing wattage even more rapidly than that of the visible region, and that in general the shorter the wave-length the higher this rate of increase in intensity *. The particular mode of variation of a line depends upon the series to which the line belongs. Even at ordinary loads the light obtainable has less of an objectionable glare than that obtainable from a diffuse arc, but with a quartz lamp operating at near red-heat the continuous background becomes sufficiently intense to cause the general colour effect to become distinctly less greenish and more yellowish.

Harrison and Forbes †, by a somewhat different method, have made a careful study of the energy distribution in the mercury arc spectra under varying conditions of load, voltage, current, and pressure. Their table of lines, being related to thermopile observations, lists, of course, only a fraction of the lines obtainable by photographic processes. Neither did the lamp used have such a constricted arc as the one under consideration here. In a later work ‡, however, they used a more concentrated arc lamp, which, while of experimental design and not especially suited for laboratory use, gave highly interesting results which have a definite bearing on the lamp described above. Their report lists certain other advantages and characteristics of such lamps of interest to those having need of a highly concentrated mercury arc, either in the physical laboratory or in connexion with photochemical processes §.

* Kuch and Retschinsky, *Ann. d. Physik*, (4) xx. p. 598 (1906).

† Harrison and Forbes, J. O. S. A. and R. S. I. x. p. 10. Jan. 1925.

‡ Forbes and Harrison, J. O. S. A. and R. S. I. xi. p. 99. August 1925.

§ For a most interesting summary of the quartz lamp characteristics and uses see Buttolph, Bull. No. 105 A, Cooper-Hewitt Electrical Company. Luckiesh (*l. c.*) gives extensive information and bibliographies.

LXXVII. *The Freezing-Points of Concentrated Solutions.—Part II. Solutions of Formic, Acetic, Propionic, and Butyric Acids.* By EDWARD RICHARD JONES, *Ph.D. (Wales)*, and CHAS. R. BURY *.

THIS work was undertaken with the object of obtaining reliable values for the activities of a few typical associated substances in aqueous solution.

The experimental methods have been fully described in a previous communication (Phil. Mag. (7) iii. p. 1032, 1927). Two Beckmann thermometers were used: the first, which was used only in one series of experiments with acetic acid (series B), has been standardized to the nearest 0·005° C. by the National Physical Laboratory; the second was standardized by comparison with the first, and was used throughout the rest of this work. The pressure corrections of the two thermometers were 0·0024° and 0·0018° C. per cm. Hg respectively.

Acetic acid was fractionally crystallized three times and then distilled from phosphorus pentoxide (Orton, Edwards, and King, J. C. S. 1911, xcix. (1) p. 1178): about one per cent. of water was added to the product to destroy any anhydride that might have been formed by this treatment. The other three acids used were purified by fractionally distilling pure commercial samples twice. The final product in every case distilled over within a range of half a degree.

TABLE I.—Formic Acid.

m.	*θ.*	*γ.*	*m.*	*θ.*	*γ.*
0·24[illegible]9	0·465	1·014	1·674	3·032	0·973
0·2684	0·515	1·016	1·930	3·475	0·964
0·3362	0·641	1·016	2·089	3·744	0·958
0·4273	0·810	1·017	2·233	3·989	0·953
0·6262	1·173	1·010	2·426	4·312	0·945
0·7599	1·419	1·008	2·675	4·723	0·935
0·9379	1·737	1·001	2·807	4·942	0·931
0·9765	1·807	1·000	2·813	4·948	0·930
1·041	1·924	0·999	3·005	5·254	0·922
1·099	2·028	0·997	3·083	5·385	0·919
1·362	2·490	0·986	3·201	5·576	0·915
1·658	3·006	0·975			

The results are given in Tables I. to IV., in the first columns of which are given the concentrations (m) in mols.

* Communicated by the Authors.

Table II.—Acetic Acid.

Series A.

m.	θ.	γ.
0·1669	0·314	1·041
0·2653	0·497	1·045
0·3097	0·578	1·040
0·3401	0·636	1·042
0·5432	1·002	1·029
0·6514	1·197	1·024
0·8247	1·505	1·014
0·8510	1·549	1·011
1·126	2·021	0·991
1·243	2·227	0·986
1·396	2·490	0·977
1·642	2·901	0·962
1·689	2·987	0·961
1·698	2·998	0·960
1·812	3·183	0·952
1·974	3·466	0·948
2·006	3·507	0·943
2·114	3·679	0·936
2·273	3·937	0·928
2·290	3·974	0·928

Series A (*cont.*).

m.	θ.	γ.
2·435	4·199	0·920
2·533	4·357	0·913
2·605	4·465	0·910
2·762	4·704	0·901
2·885	4·900	0·896
2·910	4·937	0·894
3·029	5·113	0·887
3·259	5·466	0·876
3·329	5·566	0·872
3·330	5·564	0·871
3·348	5·587	0·870

Series B.

m.	θ.	γ.
0·2811	0·526	1·042
0·8752	1·590	1·008
1·396	2·488	0·977
2·005	3·505	0·943
2·589	4·433	0·910
3·423	5·727	0·870

Table III.—Propionic Acid.

m.	θ.	γ.
0·2936	0·544	1·088
0·3126	0·577	1·083
0·4211	0·771	1·071
0·5271	0·955	1·056
0·5686	1·028	1·052
0·6606	1·187	1·041
0·8964	1·582	1·011
0·9987	1·756	1·002
1·148	1·994	0·983
1·195	2·068	0·976
1·301	2·238	0·965
1·490	2·531	0·944
1·639	2·753	0·927
1·789	2·978	0·912
2·093	3·411	0·880
2·134	3·474	0·877
2·352	3·771	0·854
2·482	3·948	0·842
2·676	4·196	0·823
2·814	4·357	0·808
2·873	4·436	0·803
3·074	4·673	0·784
3·287	4·919	0·764
3·412	5·054	0·752
3·869	5·528	0·712
3·933	5·583	0·707

TABLE IV.—Butyric Acid.

m.	θ.	γ.	m.	θ.	γ.
0·2826	0·515	1·148	1·824	2·675	0·819
0·4213	0·758	1·123	1·958	2·795	0·790
0·5809	1·028	1·092	2·100	2·888	0·755
0·8160	1·397	1·038	2·513	3·077	0·660
0·9419	1·587	1·011	3·632	3·264	0·472
1·087	1·799	0·981	3·688	3·272	0·466
1·252	2·023	0·945	4·802	3·341	0·361
1·465	2·294	0·899	5·777	3·389	0·302
1·498	2·331	0·891	9·437	3·513	0·186
1·593	2·442	0·871	13·678	3·649	0·129
1·726	2·584	0·842	17·722	3·837	0·100

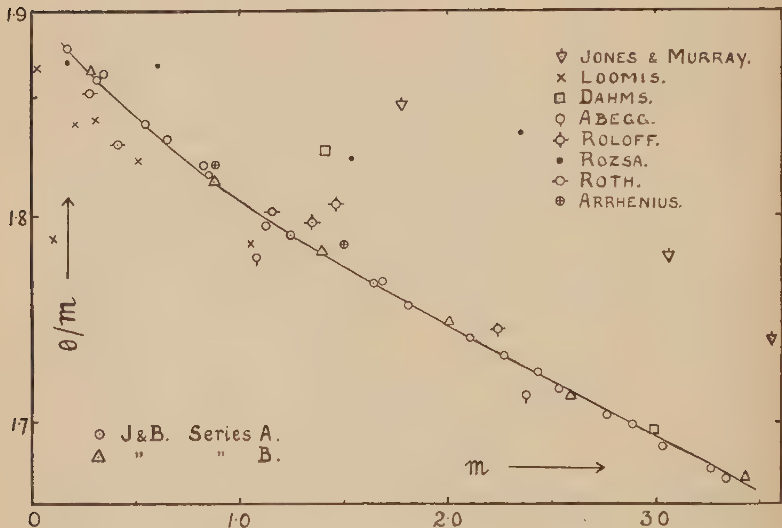
per thousand grams of water as determined by titration with baryta, phenol-phthalein being used as indicator. These concentrations are the mean of two determinations: when duplicate analyses differed by more than 1 in 500, the results were discarded. The baryta was frequently standardized against recrystallised succinic acid. In the second columns are the depressions of the freezing-point of water (θ) corrected for pressure, emergent stem, and thermometer errors, and in the third columns are the activity coefficients (γ).

Previous measurements of the freezing-points of formic acid solutions have been made by Abegg (*Zeit. phys. Chem.* 1894, xv. p. 219), Faucon (*Ann. Chim. Phys.* 1910, xix. (8) p. 70), and Jones and Murray (Amer. Chem. Journ. 1903, xxx. p. 198); of acetic acid solutions by Abegg, Arrhenius (*Zeit. phys. Chem.* 1888, ii. p. 491), Dahms (Weid. *Ann.* 1897, lx. p. 119), Faucon, Hausrath (*Ann. d. Physik*, 1902, ix. p. 548), Jones and Murray, Loomis (Weid. *Ann.* 1897, lx. p. 523), Roloff (*Zeit. phys. Chem.* 1895, xviii. p. 582), Roth (*Zeit. phys. Chem.* 1903, xliii. 556), and Rozsa (*Zeit. Electrochemie*, 1911, xvii. p. 934); of propionic acid solutions by Abegg, Faucon, and Peddle and Turner (Trans. Chem. Soc. 1911, xcix. (1) p. 685); and of butyric acid solutions by Arrhenius, Faucon, and Peddle and Turner. With the exception of Hausrath's measurements of the freezing-points of very dilute solutions of acetic acid, none of these earlier measurements are of great accuracy. Our results for acetic acid are compared graphically with those determinations by previous investigators that lie in the range of concentrations studied by us in fig. 1, where θ/m is plotted against m. With the other

acids our agreement with previous observers is of the same order.

Lewis and Randall employ the convention that the activity is equal to the concentration when the latter is zero. Calculation of activities, using this convention, involves a rough knowledge of the freezing-points down to zero concentration, which is lacking in the case of weak acids. Serious errors are caused by neglecting ionization in the more dilute solutions and by the treatment of these acids as non-electrolytes (*i.e.* by assuming the curve in fig. 1 extrapolates to $\theta/m=1{\cdot}858$, when $m=0$), though such a course is feasible,

Fig. 1.



and is recommended by Lewis and Randall ('Thermodynamics and the Free Energy of Chemical Substances,' McGraw Hill Book Co., New York, 1923, p. 290) when the experimental data are not very accurate and do not extend to very dilute solutions. On the other hand, the treatment of weak acids by the method employed for strong electrolytes is impossible without accurate data at extreme dilutions, unattainable by modern experimental methods. The convention of Lewis and Randall is therefore inapplicable, and in its place we employ the convention that activity is equal to concentration (expressed as molality) when the latter is unity. This enables a modification of Lewis and Randall's equation to be used, which avoids the difficulty

of evaluating integrals down to zero concentration. Change of convention merely involves multiplying a series of activities at different concentrations by the appropriate constant; and our results can easily be converted when the necessary data for dilute solutions are available. Since the ratio of the activities at two concentrations alone has any practical significance, the convention we have employed in no way affects the utility of our results.

The activity coefficients (γ) given in the third columns of Tables I. to IV. have been calculated from the following simple modification of Lewis and Randall's equation for non-electrolytes (*op. cit.* p. 286) :—

$$\log_e \gamma = \log_e \frac{\alpha}{m} = \int_m^{m'} -j d \log_e m - j + 0{\cdot}00057 \int_m^{m'} \frac{\theta}{m}\, d\theta + \mathrm{K},$$

$$\text{where } j = 1 - \frac{\theta}{1{\cdot}858m},$$

and where a is the activity, m' is any convenient concentration, and the integration constant K is given a value, dependent on the value chosen for m', such that our convention is satisfied.

TABLE V.

m.	γ.		
	Formic Acid.	Propionic Acid.	Butyric Acid.
0·25	1·015	1·091	1·160
0·50	1·013	1·060	1·108
0·75	1·008	1·031	1·054
1·00	(1·000)	(1·000)	(1·000)
1·25	0·991	0·971	0·946
1·50	0·981	0·943	0·892
1·75	0·971	0·917	0·837
2·00	0·961	0·891	0·779
2·50	0·942	0·840	0·664
3·00	0·922	0·791	0·557
3·40	0·907	0·754	0·500
5·00			0·347
7·50			0·235
10·00			0·174
12·50			0·141
15·00			0·118
17·00			0·105

In Table V. are given the activity coefficients of formic,

propionic, and butyric acids, obtained by interpolation at round concentrations. These activity coefficients are strictly valid only at the freezing-points of the solutions: it is desirable to calculate their values at some standard temperature (usually 25°C.), but only in the case of acetic acid are the necessary heat data available. Even here the accuracy of the data probably do not justify calculation of the change of activity with temperature over a large interval, and we have therefore calculated the activity coefficients at 0° C.

TABLE VI.—Acetic Acid.

m.	γ.	$\bar{L}_1$.	$\bar{C}_{p_1}-\bar{C}^0_{p_1}$.	γ_{273}.	$1-\alpha$.
0·005	0·937	—	—	0·942	0·938
0·01	0·971	—	—	0·976	0·956
0·02	0·995	—	—	1·000	0·969
0·05	1·025	—	—	1·030	0·980
0·10	1·035	−0·13	0·01	1·040	0·986
0·20	1·042	−0·28	0·02	1·046	0·990
0·35	1·040	−0·54	0·04	1·044	0·992
0·50	1·032	−0·80	0·05	1·035	0·993
1·00	(1·000)	−1·77	0·11	(1·000)	0·995
1·50	0·971	−2·96	0·19	0·968	0·996
2·00	0·944	−4·25	0·27	0·938	0·997
2·50	0·915	−5·66	0·36	0·906	0·997
3·00	0·891	−7·13	0·46	0·879	0·997
3·40	0·869	−8·45	0·54	0·854	0·998

In the second column of Table VI. are given the activity coefficients of acetic acid at round concentrations at the freezing-points, obtained by interpolation. In the third columns are the partial molal heat-contents of water at 17° C. ($\bar{L}_1$), deduced from the data of Sandonnini (*Atti accad. Lincei*, 1926, (6) iv. p. 63), and in the fourth columns are the partial molal heat-capacities ($\bar{C}_{p_1}-\bar{C}^0_{p_1}$) of water deduced from the data of Reiss (*Jahresb.* 1880, p. 91), quoted by Sandonnini). In the fifth columns are the activity coefficients at 0° C. (γ_{273}), calculated from the equations of Lewis and Randall (*op. cit.* pp. 289, 349).

There is a clearly-defined maximum in the activity coefficient of formic acid at a concentration of about 0·43 molal, and, apparently, a similar maximum with acetic acid in the most dilute solutions examined. To confirm the

existence of this maximum, we have calculated the activity coefficients of acetic acid at lower concentrations from the freezing-point determinations of Hausrath (*loc. cit.*). The interpolated figures for the activity coefficients at round concentrations, given in Table VI., which are based on Hausrath's data for concentrations below $0{\cdot}2m$, and on our own at higher concentrations, show the maximum very clearly. The fall in the value of the activity coefficient at low concentrations is due to ionization. There must also be similar maxima, but at lower concentrations, for the other two acids. The decrease in the value of the activity coefficient at high concentrations, where ionization is negligible, and which is characteristic of all four acids, must be due to some abnormality of the unionized molecules—possibly association.

It is often assumed that the activities of acids which obey Ostwald's dilution law are proportional to the concentrations of the unionized molecules, as deduced from electrical conductivity measurements. Acetic acid is a typical weak acid, and its solutions obey Ostwald's dilution law up to concentrations of one-tenth normal, or considerably higher if the conductivities are corrected for change of viscosity; but the assumption that activity is proportional to the concentration of unionized molecules is far from true, even in hundredth normal solutions. In the sixth column of Table VI. are given the ratios of unionized to total acetic acid $(1-\alpha)$: in calculating these, a value of $20{\cdot}4\times10^{-6}$, obtained by extrapolation from the data of Noyes (J.A.C.S. 1908, xxx. (1) p. 335) has been used for the dilution law constant. If activity were proportional to the concentration of unionized acid, the ratio $\gamma_{273}:1-\alpha$ should be independent of the concentration: it is obviously not so. The discrepancy must be partly due to the neglect of interionic forces in the usual method of calculating the degree of ionization; but probably a more important factor is the abnormality of the unionized molecules.

Butyric acid is remarkably abnormal; *i. e.* its activity coefficient changes very rapidly with concentration. This fact must be closely connected, thermodynamically, with the close proximity of the freezing-point concentration curve to the critical solution point, which lies in the metastable region within a degree of and below the curve (Faucon, *loc. cit.*). The freezing-point concentration curve is therefore in some ways analogous to the critical isotherm of a gas. There must also be some explanation of this abnormality in terms of the molecular-kinetic hypothesis, and we

think it probable that butyric acid forms micelles, somewhat similar to those formed by the soaps, as has been shown by McBain and his collaborators.

While molecular weights calculated from the freezing-points of concentrated solutions are of no quantitative value, they indicate that butyric acid is very highly associated, and that the degree of association is too great to be explained by the usual hypothesis of association to double or triple molecules.

In dilute solution, butyric acid does not differ greatly from the other three acids, but at a concentration of 1·1 m. it suddenly becomes very abnormal. This behaviour is particularly clear in comparing the curves obtained by plotting j/m against m and used in evaluating activities. This sudden departure from the normal is also characteristic of the soaps (McBain, Randall, and White, J. A. C. S. 1926, xlviii. p. 2517), and is a natural consequence of the law of mass action when applied to the association of simple molecules to form complex molecules containing a large number of single molecules, such as these micelles are.

The soaps and butyric acid have one feature in common which is probably essential for micelle formation: they both consist of long molecules, one end of which—the hydrocarbon end—has little attraction for water, while the other end—the COONa or –COOH group—has considerable attraction. In other respects there is little resemblance between the soaps and butyric acid: the former are strong electrolytes and form ionic micelles, while butyric acid is a weak electrolyte and less than 1 per cent. ionized at concentrations where micelles exist.

We hope shortly to offer further evidence in favour of this hypothesis.

One of us (E. R. J.) wishes to acknowledge his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant during the session 1925–26, and to the University of Wales for a Postgraduate Studentship during the session 1926–27.

Edward Davies Chemical Laboratories,
University College of Wales, Aberystwyth.
May 26th, 1927.

LXXVIII. *Discharges and Discharge-Tube Characteristics.*

By WILLIAM CLARKSON, *M.Sc., A.Inst.P., Armstrong College, Newcastle-on-Tyne* *.

Introduction.

THESE experiments, carried out in the session 1925–26, were undertaken on account of certain observations made during a study of "flashing" in Argon-Nitrogen tubes over a wide range of pressures [6], these observations showing that "flashing" must be of universal occurrence in electrical discharge-systems, in virtue of the fact that all such systems possess "sparking" and "extinction" potentials, and have capacity.

It was found possible to obtain discharges of two kinds: "flashes" in which the characteristic was only finally reached, and discharges in which the characteristic itself was traversed, only dynamic equilibrium being attainable in the former type.

An examination of discharge-tube "characteristics" proved that discharges of quite unique appearance were associated with each stage at whatever pressure, the positive column being present, and further that valuable information could also be gained from observing the appearance of "flashes," either directly or in a rotating mirror, the latter serving to resolve the phases of complex discharges.

The following paper gives the general association of discharges with discharge-tube characteristics; but though it was possible to correlate many references in the literature of the subject [1] to the discharges observed, so much has been done, especially in publications in German, that the need no longer exists [2,3,10].

A reference to some of the ideas employed may not be out of place here, especially as many are not being fully developed till later. The idea of a "threshold current" [12] was constantly utilized, the "sparking potential" under dynamic conditions being taken to decrease with the "initial current," but the full significance of this was not demonstrable until the correspondence of the "statical sparking potential characteristic" with the "corona characteristic" was discovered [4]. Also, though a "slow build-up" was implied by many phenomena, this could not receive closer attention till recently, when the "corona-lag" was investigated [5], and here the effect

* Communicated by Prof. G. W. Todd, D.Sc.

of the "clear-up" has been limited in the main to the problem of "overlapping" in "flashing."

These ideas will be treated in more detail after the "characteristics" have been considered, and then an account of representative experiments will be given.

Tubes and Apparatus.

For the most part the experiments described here were carried out on two tubes, air, nitrogen, or argon-nitrogen mixture (this giving lower sparking potentials) being employed in a dry, though not a pure, state. It was not considered necessary to use absolutely pure gases, and later experiments have proved that the results obtained also apply to tubes of scrupulous purity. Though pressures up to a few millimetres were generally used, the range was extended to half an atmosphere, without, however, exceptional phenomena being encountered.

It was desired to have tubes of large cathode area, so that the extent of the negative glow could be studied, tubes that were free from wall effects, assuming these to have an influence, and with the discharge always taking place in the same region, this preventing the rapid change in critical constants so noticeable in tubes where the discharge can occur in different places. Movement of the discharge also inhibits visual examination. To this end the smaller tube was made with electrodes placed axially in a cylindrical tube some five centimetres in diameter. The electrodes were 10 cm. long, and consisted of brass rods one cm. in diameter, with hemispherical ends; their separation never being more than a few mms. This tube was especially good for mirror observations and for the variations of the negative glow. Later, a second tube was made, with convex brass electrodes 15 cm. in diameter, the upper electrode being movable. The maximum separation was 15 cm.

The electrodes were smooth and highly polished, but though all the apparatus was chemically clean initially, a high degree of electrode cleanliness could not be maintained, probably owing to the active nature of the gases present, particularly oxygen.

All discharges in these tubes were axial and the tubes were satisfactory in every way.

Constant potential up to one thousand volts was generally obtainable, batteries and an M.L. Anode-converter being used; but often, as when using a diode at saturation current, or when slight voltage variations did not matter, the 480 D.C. mains could also be employed.

Though resistances were often used, a diode (valve with grid and plate connected) was often employed to give a constant current system. In this respect the work differed greatly from previous work in which only a constant resistance had been used.

Voltages were measured with an electrostatic voltmeter, normal range 200–600 volts, but this was altered when necessary by putting batteries in series. When maximum and minimum voltages were being measured a diode also was included, as previously[6], and a small capacity placed across the voltmeter to lessen the effect of leakage.

General Considerations.

Current-voltage characteristics.

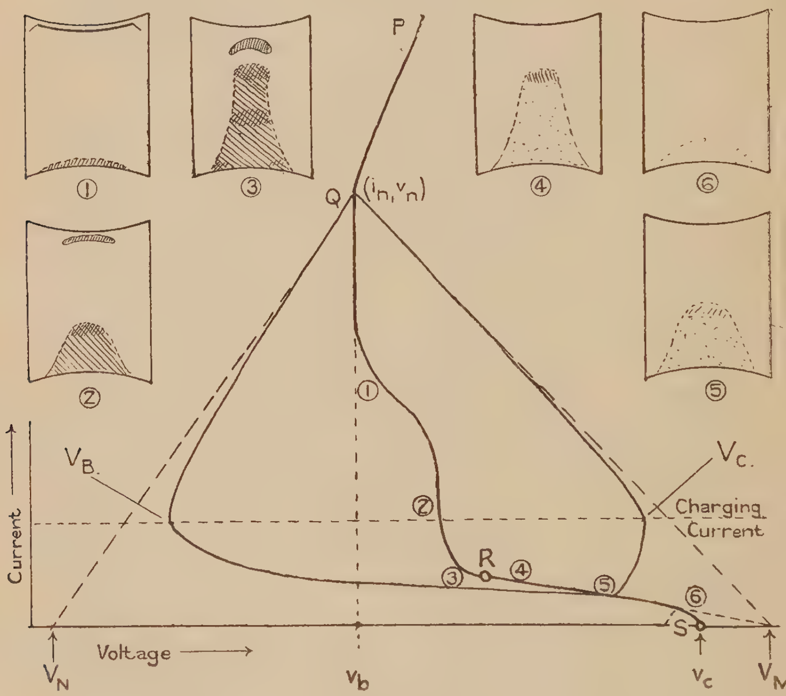
As this is a property of discharge-tubes that will constantly be referred to in this paper, its form in the tubes just described must first be considered. Under all conditions the characteristic was invariably of the form given (schematically) in fig. 1, though the actual values of the voltage or the current depended not only on the pressure and nature of the gas and on the electrode separation, but also on the state of the electrodes.

The characteristic (fig. 1) fell naturally into two sections: PQR the "stable" region and RS the "corona" region. PQ is the normal characteristic, Q giving the minimum voltage v_b at which the discharge could be sustained. From Q the voltage increased with increase of current. With decrease of the current, though the voltage might be constant for a certain range, below this range a fairly quick rise (10–50 volts) occurred until another constant range was reached (down to R). At R another short quick rise in voltage took place, the "corona" characteristic was entered, and generally intermittence set in, even with minimum capacity. Indeed, in these tubes the "corona" region was seldom stable enough for the voltages to be measured; but sufficient results were obtained to show that the characteristic, as expected, was of the same form as in other tubes, and that the flattening of the characteristic at R was continued in a gentle curve to the region of the statical sparking potential S, at which value the voltage remained constant down to the lowest appreciable currents.

The "corona" characteristic has also been referred to as the "threshold characteristic"[4], because it represents the minimum current (or space charge) from which, at the voltage esent, the current can increase (build-up). The fact that,

in these experiments, a greater residual space charge or current was accompanied by a lower dynamic sparking potential is in accord with this view of the "corona" characteristic, and though it cannot be proved, it seems highly probable that the statical threshold current conditions hold fairly closely even in rapid intermittence, even though the equilibrium here is dynamic. This view will be accepted provisionally in this paper, just as the "stable" characteristic will be assumed to hold also.

Fig. 1.



Discharge and Characteristic.

------ "Single Flashes" ——— Intermittence

Single Flashes.

The course of a single "flash" or condenser discharge may now be followed. If a condenser charged to a voltage V_M is applied to a discharge-tube a strong discharge occurs (save in certain circumstances) and the voltage falls to a value (V^N), lower than v_b. The intensity of the "flash" and the extent of the negative glow depend on the size of the capacity and can serve as indicators of the current attained. Since the

discharge starts at some point ($i=0$, $v=V_M$) on or to the right of the corona characteristic and finishes at some point to the left (0, V_N), it must have intersected the stable characteristic, and further, since it starts and ends with zero current, the current must undergo a period of increase and then of decrease. If we assume that the maximum current is attained, as is probable, at the "stable" characteristic, the intercept in each case may be determined at least approximately.

With a capacity (C) across the tube a steady current is caused to flow and the point i_n, v_n on the characteristic is attained. If now the circuit is broken the discharge ceases but the voltage of the capacity has fallen to a value V_N. The difference between v_n and V_n is a measure of the "clear-up" for that point on the characteristic. In this way the whole characteristic may be examined for small capacities, and to a less extent for large ones, for though nearly all the characteristic is stable for small capacities the minimum current at which a discharge can be maintained increases with the magnitude of the capacity. When we know the i_n, v_n corresponding to the V_N for the single flash, we have some idea of the point at which the stable characteristic was reached.

Experimental results gave that $v_n - V_N$ increased as i_n, v_n increased, a lower final voltage thus implying a higher maximum current, the capacity of course being constant.

If a diagram is drawn, as in fig. 2, V_M, v_n, and V_N may all be inserted, and if they are joined a schematic plan of the path of the discharge is obtained, neglecting for the moment the problem of "clear-up" mechanism, a point to be returned to later. The straight lines are merely diagrammatic.

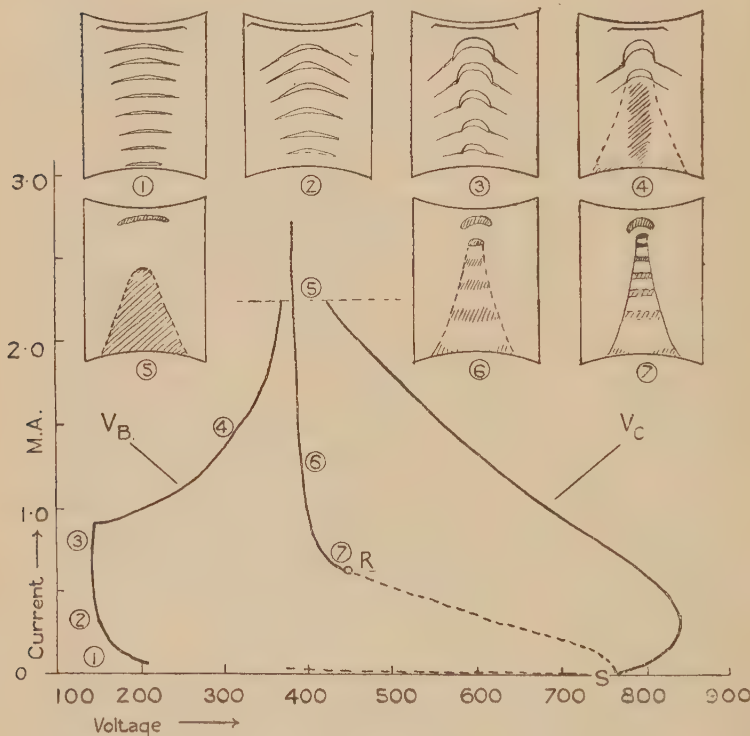
"Dynamic characteristics."

The following views have been implied in this account. The characteristic is assumed to lie between two regions where only dynamic equilibrium can be attained, but whereas to the right the factors tending to increase the number of ions predominate, to the left the reverse is the case, the characteristic forming the boundary where the influences are equal and statical conditions hold. P–Q determines the maximum (steady ?) current possible at any voltage, as imposed by the tube constants, and QRS determines the minimum value, this only being stable when the current is limited by the external circuit, since in all cases the current will attain a maximum value.

Another assumption [5] that will be made is that concerning

the variation of current with time, a variation of which fig. 1 can give no idea. Here it is assumed that the current takes some little time to attain its maximum value, increasing at first slowly and then more and more quickly, a reverse process taking place on "extinction." These are necessary assumptions for the explaining of "corona" lags and many other properties of condenser discharges.

Fig. 2.



Intermittent Discharge ($C = 5 \times 10^{-6} \mu F$)
Nitrogen, 4 mms. press.

By "extinction" is meant the leaving of the characteristic for the region of the unsustained discharge. "Extinction" must occur when a condenser discharge reaches the characteristic between Q and S, as further passage of current must reduce the voltage below that value required by the sustained discharge. If this is the sole mechanism of extinction, it would imply that the discharge could not

"go-out" in the section P–Q, as here it should be possible to traverse the characteristic down to Q before this occurred. If this traversal was rapid enough (a questionable point), though the maximum current as determined by the characteristic would be carried, excess of space charge representative of the higher current might still be present when Q was reached, in which case "clear-up" phenomena would be explained. Certainly the region P–Q is traversed when a suitable resistance is in series with the condenser.

It would appear, however, that "extinction" actually can occur even in discharges where there is a charging current greater than Q. "Hysteresis" has been invoked to account for this and for the fact that "extinction" occurs in cases when a steady current is suddenly reduced—a case parallel to that of condenser discharges. An objection to "extinction" on PQ is that it implies that the tube can carry "clear-up" currents greater than the maximum currents permitted by the characteristic, in which one would have to postulate that the characteristic gave merely the maximum steady current or that the normal characteristic did not apply to flashes where lags in the cathode fall were so pronounced.

In this paper it will be accepted that "extinction" occurs at the intercept, such an assumption being easier to handle and not seriously affecting the experimental conclusions.

Intermittence.

Each individual discharge in intermittence may be taken to present the features of a single "flash" modified by a charging current, this causing the condenser voltage to increase whenever the current in the tube is less than this current in the circuit, that is to say, in the first stages of "build-up" and the last ones of "clear-up"[5], when of course maximum and minimum voltages (V_C and V_B) will be attained, though the general variation may be inferred from several ways; but it is impossible accurately to determine i_n, v_n in the absence of an exact value for V_M. Fig. 1 gives the new discharge path implied, and it will be seen that if the rate of charge of the condenser is great enough (i large or C small), and the "clear-up" current sufficiently large, it is possible for a current still to be flowing when the corresponding voltage v_m on the characteristic is reached. If the intersept is on the "corona" section another "flash" will occur, but if it is on the "stable" section at a point for which a steady current is possible for the capacity with the given charging current, a continuous discharge will ensue,

even though this may not happen until after several "flashes." It is easily seen that for this condition to be attained the charging current must be greater than the minimum steady current—an experimental fact in intermittence.

Experimental.

Appearance of Steady discharges.

An account of the voltage-current variations of the full characteristic has already been given. Generally the current was varied by altering the filament current of the diode regulating the circuit current, the voltages being given by the electrostatic voltmeter across the tube, with or without a diode in series with it. The electrode separation was always great enough for a positive column to be present at some stage of the discharge and, as already has been said, the visual appearance of the discharge was a sure index to its relative position on the characteristic ; so a general account may be given that will apply to both tubes under whatever conditions.

At the smallest currents, at v_c on the "corona" characteristic, the only visible evidence of a discharge was a faint glow at the anode, this glow increasing in brightness and depth as the current increased and often developing a bright head [3], which at the final stages became an elliptical bulb. At R, the transition to the stable characteristic was made, and the positive column, in the few cases where this stage could be maintained, filled the interelectrode space with a confused glow.

The transition was marked by the sudden appearance of a strong though limited negative glow, this glow being cupped round the end of a positive column similar to, though more distinct than, that preceding the transition. With increase of the current this column decreased in length and in distinctness, and the negative glow moved to the cathode and occupied a greater and greater amount of its surface. At last, when Q was reached, even the last traces of an anode glow had generally disappeared and only a bright, thin negative glow remained. From this point the discharge merely gained in intensity as i was increased, save at higher pressures when the usual steady striæ appeared. The length of the column in a tube was of course also determined by the nter-electrode distance, and its distinctness by the pressure, the definition increasing as the pressure increased. The discharges typical of "flashes" are discussed later.

Though such phenomena made it possible to study discharges by visual observation alone, this method was of limited application in that it could not differentiate the actual phases in a discharge or series of discharges. Consequently a rotating mirror was utilized. A silvered microscope slip, polished on the outside, affixed to an electric motor of regulatable speed proved quite adequate.

When the discharge was very narrow, as in the rod tube, or if a slit was used, "flashes" up to many thousands per second could be resolved. Thus the mirror served to detect intermittence, though head-phones and a wavemeter were also employed to this end. Frequencies giving notes beyond audio-limit were frequently encountered.

"Flashes" and Intermittence.

It was found that condenser discharges in these tubes could be classified in two groups: those which ended on the "corona" characteristic ("corona" flashes), and those ending on the stable characteristic ("normal" flashes and sparks).

The spark was the form of the normal "flash" for high current densities, occurring with large capacities or at high gas pressures, the positive column here becoming extremely localised. Its intense nature was demonstrated by pitting of the electrodes, and in more extreme cases by the complete discharge of the condenser. Its other properties will be dealt with when discussing the normal form of "flash."

The presence of a positive column in "flashes" showed that this phenomenon was also manifested in traversing the region to the right of and between the "corona" and stable characteristics. Such a column was always striated, the number of striations being related to the voltage across the tube, that is to say increasing with pressure and electrode separation, and suggested that the striæ were, to a first approximation, about an ionizing potential apart. In many ways they were reminiscent of the striæ observed under certain conditions on the corona characteristic in the rare gases, but such striæ were never seen in these experiments.

The striæ were best observed in not too slow "flashing" as they were continuously in evidence, but in all cases the duration of "flashes" was too short for the variation of the striæ with time to be studied directly. Fig. 2 shows their change in shape when a constant capacity and a steadily increasing charging current was employed, which here implies also greater initial currents in the tube and the accompanying lower dynamic sparking potential, and from this an idea of their dependence on voltage and current may

be deduced. We may attribute the striæ observed to the slower portion of the build-"up," since it is here that they will exist for the longest time and despite a probably lower intensity will have a greater visual effect. In the corona striæ just mentioned the striæ were flatter and thinner at small currents, but became increasingly domed and lenticular as the current increased, and we may expect the same changes in the inter-characteristic region.

The same variations with tube-current and voltage for "flashing" striæ will be observed in fig. 2, but it will be seen that more extreme forms were developed; thus the final form consisted ot a cup-like "core" with side "wings." According to the views advanced in this paper, the condenser voltage would only slightly increase in attaining V_C when large initial currents were present and the striæ exhibited would be those corresponding to all the stages from small currents up to quite large ones at but a slightly higher voltage. These would appear superimposed and would be of the form observed, the "wings" corresponding to the initial stages and the intense "dome" to the final stages.

Even in the initial stages of "sparks," when the "core" of the discharge was just a glowing column these "wings" were still observable, an observation in complete accord with the opinions just advanced.

If a sequence of two discharges occurred at different initial voltages their difference was immediately demonstrated by the appearance of two (superimposed) sets of striæ in the tube, the presence of a steady stage being recognizable in a like manner, even without the assistance of the rotating mirror.

Fig. 2 shows the variations of Vc and V_B, and the appearance of the discharge for a small capacity, that of the large tube alone, with the current increasing from zero up to the value at which the discharge became continuous (0–5) after which the current was reduced until intermittence again set in (5–7). Three stages of "flashing" were recognizable: (0–1) a region of "corona" flashes, these always occurring when the charging current was not great enough for the discharge to win clear of the "corona" characteristic; (1–3) the region of the "striations"; and (3–5) a "final" stage[11]. From (0–1) the voltage readings for V_C and V_B were somewhat erratic and in consequence have merely been indicated. From (1–3) the "flashing" was quite regular, a steadily increasing frequencybeing recorded as the current was increased; but though V_B changed very little, V_C at first rose rapidly, and then as the charging current became still greater, gradually

diminished. At this stage the frequency was of the order of a thousand or so per second. A sudden change in pitch and an abrupt increase in V_B heralded the next stage (3–5). V_B increased rapidly at first and then slowly attained a value rather greater than v_b,—V_C still falling, though without evidence of discontinuity,—until finally there was only about 20 volts difference between them. The frequency was now generally at or beyond the audio-limit.

With further increase of the current the discharge became steady, and it was seen that a point about midway on the vertical part of the stable characteristic above R had been attained. As has already been said, the voltage did not change much as the current was reduced until this had almost attained its minimum value, at which stage it rose and intermittence supervened.

These phenomena can readily be explained on the assumptions already outlined in this paper.

V_C varies according to two factors, the charging current and the "initial" current in the discharge. The second effect cannot be present until a certain frequency is attained, after which it plays a dominant role, and the initial voltage v_m traverses the whole of the "corona" characteristic as the frequency increases. The extent of the negative glow showed, as is to be expected, that the intercept on the "stable" characteristic at first increased and then decreased, V_B not suffering much change until (5) was reached. The sudden rise of V_B would be explained by the intercept moving onto the region between Q and R; it would rapidly leave the more horizontal part and would finally reach the more constant voltage part. The appearance of the discharge supports this explanation.

As the difference between V_C and V_B was very small at the "final" stages, the time spent near or at the stable characteristic would represent an increasing fraction of the time of discharge, and we may expect the phenomena of this region to come into greater prominence at this stage, and the positive column to increase with the charging current on account of the steadily decreasing intercept. Such a region is, of course, not easy to study, as the discharge is in the neighbourhood of both sections of the characteristic all the time, but the discharges discussed here certainly were intermittent and not merely pulsatory.

Interrupted "Steady discharges."

Very interesting observations were made during a study of discharges, whether finally steady or intermittent, before

they had attained regularity. The charging circuit was made and broken at regular intervals at a frequency suitable for the rotating mirror, a mercury interrupter being used for this purpose.

Where the current was such that only intermittence could occur it was seen that, as expected, the "flashes" were not necessarily alike until after several had taken place. The first "flash" was the strongest as it commenced at v_c, and if "overlapping" was present to any appeciable extent, this was followed by a succession of fainter "flashes" at steadily decreasing time intervals, until finally they occurred regularly and had the same brightness, showing that a constant dynamic sparking potential had been attained. Naturally this was only observable in full when a sufficient number of "flashes" could take place between breaks, that is when the "flashing" was of high enough frequency.

The phenomena when the current was large enough to result in a steady discharge were very illuminating. Though a large capacity only gave "flashes," the discharge showed two "flashes" as C was reduced, the first strong though not reaching so high a current as for the larger capacity, and the second weaker. This was then followed by a steady discharge, the point R having presumably been reached during the "clean-up." With smaller capacities only one "flash" was necessary before steadiness was reached, smaller maximum currents being recorded. The presence of a gap between the "flash" and the steady discharge (a noticeable feature in all these cases) would agree with the explanation that the stable characteristic was departed from and returned to again (at R), and though it could conceivably represent the traversal of the characteristic, this is believed to be a distinct case and will be considered later. Such an explanation would scarcely account for the time interval observed.

"Flashes" ending in a discharge, whether constant or transient, on the characteristic, were generally readily distinguishable, the negative glow at low currents being of limited area and standing off the cathode, so that two cathode glows were seen on looking at the discharge, even though the positive column was masked by the striæ. Their extent and brightness gave a very fair idea of their relative duration.

Induction-coil discharges.

Similar phenomena were obtained on the large tube with pressures up to half an atmosphere, a large induction coil being used as a transformer for the alternating mains. An

Amrad "S" tube was found to make a very satisfactory rectifier. In these cases the "normal" characteristic gave the usual striated positive column for all currents greater than Q.

In the rotating mirror the discharge was seen to consist of a spark[9], or series of sparks if the condenser was large, followed by a gap (clear-up), and then the gradual emergence of striæ from the anode. The current at this stage was increasing, as the increasing negative glow clearly showed, but whether the characteristic was retraversed when the current decreased seemed to depend very much on conditions. It is probable that the rate of reduction was the determining factor. It is of interest that oscillograph records of such a discharge in a mercury lamp[8] suggest that a similar explanation may be applied to that case also.

Special study was made of the gap between the "flash" and the steady discharge, as it was initially thought that this was due to a retraversing of the characteristic until the tube current equalled the charging current; but the evidence suggested that this was not so, neither anode nor negative glow being present.

When an ordinary induction coil was used the difference between the currents in opposite directions was most interestingly shown, the one giving merely a series of sparks but the other finally ending in a steady discharge.

Discharge of Capacity through Resistance.

Though reasons have been advanced for supposing that "extinction" often occurred at the point of intersection of the characteristic, definite evidence of the traversal of the characteristic from this point under certain circumstances will also be given. This traversal was particularly in evidence in condenser discharges through a resistance, both for single "flashes" and for intermittence. Indeed the characteristic itself was occasionally studied in this way, a large (10μ. F.) condenser being charged to a high potential and discharged through the tube in series with a suitable high resistance, such a discharge of course resembling the discharge of a battery on decreasing potential.

In such a system though the passage of a current must lower the potential of the condenser, the same does not apply to the potential across the tube, as this is able to increase under certain circumstances, for, since the

potential fall along the resistance is determined by the current, which in turn is fixed by the tube characteristic, its value will also decrease with time. If this rate of fall is greater than that of the condenser, the tube potential will increase. The action of the resistance is thus to permit an accommodation of the voltage across the tube to the tube characteristic, as was clearly demonstrated when, for such a system, the charging circuit was suddenly broken.

The phenomenon of these "flash-steady" discharges was also observable in intermittence where a resistance of suitable size was interposed between the condenser and the discharge-tube, the possibility of this form being obtained and the duration of the "steady" portion increasing with the capacity and the resistance. The fact that there was often an abrupt transition from normal "flashing" to the "flash-steady" form at a certain stage of the increase of capacity suggested that the two forms were quite distinct, though at other times it did appear to be possible to effect the transition more gradually. Visual observation showed also that the resistance sensibly limited the current attained, the time of the "flash" thus being increased, so that altogether discharges of appreciable duration were produced; in fact, it was possible to have intermittent discharges in which the dark interval was very small in comparison with this period. In the case where the resistance is in the condenser arm, a further influence will be that the "flash" will be due to the capacity of the tube alone until the voltage has dropped to a value much less than that of the condenser.

Tubes of low conductivity were not studied, but previous work showed that "flashes" of longer duration also occurred in these tubes, particularly with the larger capacities [7].

It will be seen that all these factors increase the possibility of a stable state being attained. Indeed they have been utilized in work on this question [7].

One problem arising from the study of such discharges was whether the normal characteristic was traversed in all cases at the end of a "flash," and to what extent, the duration of such a traversal of course being calculable, in the case where no resistance was employed, from the voltage fall and the average current. Usually the time required in these experiments was so short that it would not have been observable, and thus there was no visible proof that this did not always occur. Before any change could be noticed in a mirror it would be necessary for a

small current stage to be reached, and this from the positive glow present was what happened in "flash-steady" discharges, the restricted negative glow accompanying this stage also being a prominent feature. A gap between the "flash" and the "steady" sections would indicate that extinction had occurred, the clear-up region giving small currents with an absence of a distinctive discharge, but only when it could be proved that the charging current was greater than that at Q (fig. 1) was it possible to have direct evidence suggesting that extinction might occur on the normal characteristic and that traversal of the characteristic did not usually take place.

Inductances.

The effect of large inductances in the condenser arm was also examined. As expected, due to the potential absorbed as the current changed, they encouraged the production of a series of "flashes" of decreasing intensity, damping out the "build-up" and quickly restoring the voltage during "clear-up." The number of "flashes" in each discharge changed as the capacity was altered, and it is certain that the "flashes" represented discharges of the tube capacity in a great number of cases. Such a possibility has already been considered and further comments are therefore unnecessary.

Pulsatory and similar discharges.

Though in these tubes the discharge was confined to the middle of the electrodes and "fatigue" effects could not effect a large movement of the discharge, rotating mirror examination showed that great fluctuations of the negative glow occurred even in discharges which apparently were quite steady. The specific part these might play in instability at lower currents was not studied, but it is probable that they were not without influence.

Sometimes when the discharge had nominally become steady, as in fig. 2, the mirror showed that the discharge was definitely pulsatory, the positive column and the negative glow going through a regular sequence of changes, the discharge varying from merely a strong negative glow to the restricted glow and strong positive column (the range between Q and R?). The frequency varied as in normal "flashing," with C and i, but the slow frequencies gave the greatest changes in appearance. These discharges appeared never to be extinguished and were quite distinct from "flashing," giving no sound in headphones or wavemeter, rapid and extreme changes of current thus being

absent. Though the discharge became steady in the sense given in the preceding paragraph, no discontinuity occurred with increase of current.

It is significant that when "flashing" was studied in the case where this was observed a variety of "flash-steady" discharge was seen with the larger currents. In the mirror the "flash" was followed by a regular movement of the negative glow from the cathode until finally it merged into a positive column and the discharge ceased. Such discharges were not to be confused with the behaviour of the negative glow in "clear-up"[3], or the occurrence of a second incipient "flash." Corona "flashes" were more readily obtained in these cases also.

These effects are reminiscent of those obtained with resistance in the capacity circuit, or for limited conductivity, and may be attributed to electrode effects producing discharges very similar to those "preliminary discharges" described in connexion with the "corona lag."[5] In many ways the resemblance between these pulsatory discharges at the vertical region of the "stable" characteristic, and "corona flashes" at the vertical region of the "corona" characteristic, was very close, but it is similarly not easy to explain them without invoking great changes in the characteristic unless it is assumed that they really were intermittent. We may assume that the voltage would always be about constant, and that the characteristic was never much departed from owing to the strong retardation. The discharges would then be those of the characteristic and the "dark interval" would be inappreciable as in many "corona" discharges. The "flash-steady" discharge would also be explainable on this basis.

It is certain that more rapid and extreme discharges of this nature, such as would occur with smaller retardations, would affect telephones, and indeed blurred notes that could be attributed to such discharges were occasionally heard. Such notes may be heard in some "flash-steady" discharges near the critical resistance. It is always possible, of course, for discharges determined by the capacity of the tube to be superimposed on "flashes" due to a condenser, as in the cases previously given.

"Steady" striated column.

It was not always easy to study the striated positive column at the lowest steady currents, as this region of the characteristic was often very unstable even on the capacity of the tube alone. This was probably due to the

action of impurities either in the gas or on the electrodes, a slight trace of oxygen in nitrogen having an appreciable effect in this direction, even without seriously affecting the voltages.

Fig. 2 gives an illustration of the form this discharge could take, and though the final form was not always obtainable, this must in part be attributed to the instability referred to, though it is true that great differences in definition existed in different cases. Once the hazy column had assumed a definite form increase in current merely caused the details of the column to become more clearly defined, the end striæ taking the form of flat plates at regular intervals. At the lowest currents they increased in number as well, as the voltage increased, and the cone became crossed with thin flat striæ which decreased in distinctness towards the anode. The negative glow now almost enclosed the tip of the positive column.

Where a mixture of gases was present the striæ showed stages of clearness and vagueness as the voltage changed, the colour of the striæ depending on the gases present.

The mirror was used to determine whether the striæ were moving striæ, but rather unsatisfactory results were obtained. The striæ at the tip of the column seemed always to be steady, but those near the anode were fluctuating in a regular manner. Occasionally they were seen to flow, but this was due to a change in current, just as the fluctuations could be due to variations of the discharge due to "fatigue" effects.

Where the rod tube was employed the discharge moved into the weakest field and very unsymmetrical columns were obtained[10]. The field also had a great effect on the form of the striæ in "flashing." With a pointed cathode and a plane anode the "wings" almost disappeared[11], but with a reversal of these conditions they formed one large dome with the rest of "core," the striæ increasing rapidly in size with nearness to the cathode. This is the form present when a "flash" takes place from a limited area of the anode.

In conclusion the author would like to express his sense of obligation to Professor Todd, Armstrong College, for his constant support in his researches, and to the Board of Scientific and Industrial Research, whose award of an Investigatorship permitted these and other researches to be carried out.

Summary.

An account is given of discharges in gases up to half an atmosphere pressure, the positive column being present. The appearances of the discharges are employed in explanation.

1. A common volt-ampere characteristic was found, a unique discharge being associated with each stage at whatever pressure.

2. A condenser discharge is considered as a jump from the "corona" characteristic to the "stable" characteristic, "build-up" occurring from the first and "clear-up" beyond the second. The characteristic is thus considered as a statical boundary between two regions where only dynamic equilibrium is possible.

3. "Threshold current" phenomena and "clear-up" effects are discussed, and are employed to explain dynamic sparking potentials.

4. The various ways in which a discharge can become steady are developed and the problem of "extinction" considered.

5. The variations of striæ in "flashing" are recorded and associated with the lag in the "build-up."

6. These assumptions are applied to discharges of many kinds observed or in references.

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LXXIX. *Notices respecting New Books.*

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, et de Technologie. Vol. V. Années 1917–1922. Deuxième Partie. Pp. lii + 805 to 1934. (Paris: Gauthier-Villars et Cie. 1926.)

THIS volume completes the publication of data for the period 1917–1922. The arrears of publication arising from the war are gradually being overhauled, and the next volume, dealing with the years 1923–1924, should shortly be ready. A detailed index for the first five volumes is also in course of preparation. The volume for the years 1925–1926 is promised for 1928, and thereafter the publication will become once more an annual one.

The arrangement of the present volume is similar to that of preceding volumes with few exceptions. Photochemistry has been given a separate section. The section dealing with photography has been considerably expanded and contains a mine of information. The method of classification of alloys in the metallurgy section has been changed.

The tables are not in any sense critical; that is not their purpose. They provide a valuable reference medium for numerical data in all branches of science, and no well-equipped scientific library can afford to be without them. It may be added that eighteen countries have contributed to the cost of preparation, through subventions from the Government, scientific or technical societies, and industrial firms.

A Treatise on the Mathematical Theory of Elasticity. By A. E. H. Love, M.A., D.Sc., F.R.S. Fourth Edition. Pp. xviii + 643. (Cambridge University Press. 1927. Price 40*s.* net.)

The third edition of Prof. Love's well-known and standard treatise on the Mathematical Theory of Elasticity appeared in 1920. The new matter included in the present edition is not very extensive, amounting only to about 20 pages. The most important additions are: (i.) a simplified treatment of the equilibrium of a sphere, leading by elementary methods to the most important geophysical applications; (ii.) a discussion of the theory of the bending of a rectangular plate by pressure applied to one face; (iii.) a discussion of the theory of large deformations of plates and shells; (iv.) an account of the process by which stress-strain relations are deduced from the molecular theory of a crystalline solid. Other minor additions or revisions have been made where necessary.

The numbering of the articles in the earlier editions has been retained—a procedure which is to be commended. Articles added in earlier editions were designated with the suffix A or B:

those added in the present edition have been marked with suffixes beginning with C. Under (i.) above, renumbering of some articles was necessary. In this connexion it may be pointed out that in § 180 the reference to § 184 should have been changed to § 177.

The frequent revision of a standard work of this nature is desirable, so that the results of new researches may be incorporated. Prof. Love has been very successful in doing this without unduly increasing the size of the book. It is likely to remain the standard work on the subject for many years.

The Polarimeter, a Lecture on the Theory and Practice of Polarimetry. By V. T. Saunders. (Adam Hilger. 1*s.* 6*d.*)

The author gives an interesting historical account of the development of the polarimeter from the earliest efforts to the standard instruments of the present day. The Lippich type of polarimeter is described in detail. "The Polarimeter has exerted a great influence upon the progress and development of the theory of organic chemistry," and in this connexion reference is made to Pasteur's work on tartaric acids, to the use of the instrument in the sugar and other industries, and lastly to its practical application in biological research.

Elementary Algebra. Part 2. By F. Bowman. (Longmans, Green & Co. 1927. 6*s.*)

The second part of this work deals with the three primary series binomial, exponential, and logarithmic, with an introductory account of the convergence of series in general. The chapter on Graphs brings under consideration algebraic functions of higher degree, the circle and radius of curvature, confocal conics and Cassini curves, followed by the treatment of complex numbers and conformal representation. The final chapters are devoted to the solution of equations of the third and fourth degrees, to determinants of any order, and the solution of simultaneous equations. The numerous examples and exercises—about one thousand, mostly with answers—will be found very useful to the student.

Principia Mathematica. By A. M. Whitehead and B. Russell. Volume 2, 45*s.*; volume 3, 23*s.* 2nd Edition. (Cambridge University Press.)

The Cambridge University Press has now completed the second edition of the important work, 'Principia Mathematica,' by Prof. Whitehead and Mr. Bertrand Russell. This work has remained since its publication in 1906 the most important work on the foundations of Mathematics, and in all probability it will contiuue

to be so for some considerable time. The volumes at present under review are concerned with Cardinal Arithmetic, Relation Arithmetic, Series, and Quantity. These two volumes constitute, as before, a triumph of printing.

The Upper Palæolithic Age in Great Britain. By D. A. E. Garrod, B.Sc. Pp. 211, with 49 figures. (Oxford: Clarendon Press. 1926. Price 10*s.* 6*d.* net.)

A very useful service has been rendered by the author in collecting together records of the Upper Palæolithic industries of Great Britain. Hitherto the literature relating to them has been buried for the most part in various scientific journals, some of which are not easy of access. In addition, authors have varied considerably in their system of nomenclature, and the collections themselves are scattered through various museums and private collections.

A systematic review of the available material was therefore necessary in order to correlate the whole of the material and to gain the correct perspective. The author has performed her task well, and this volume will be invaluable to the investigator who attempts to compare the palæolithic industries of Great Britain with those of other countries.

A full account is given of the Upper Palæolithic cave-sites and of the different implements, bone and other objects and fauna found in them. This is followed by a description of open-air finds referable to Upper Palæolithic times and of epipaleolithic cultures. A chronological table of Upper Palæolithic sites and a complete bibliography and index enhance the usefulness of the volume for purposes of reference.

The Stone Age in Rhodesia. By Neville Jones Pp. xiv + 120, with frontispiece in colour and 40 figures. (Oxford: University Press. 1926 Price 12*s.* 6*d.* net.)

South Africa promises to provide an unrivalled field as a scene of prehistoric study. At present very little has been done to investigate the relics of palæolithic times. The late Dr. Péringuey, Director of the South African Museum, Cape Town, and the late Mr. J. P. Johnson in the Union, and the Rev. Neville Jones in Southern Rhodesia have made the most important contributions. The purpose of the present volume is to place on record all that is so far known of the Stone Age in Rhodesia and to stimulate interest in a study which, in the opinion of the author, only lacks popularity by reason of its being so little comprehended.

Difficulties of classification in South Africa, when an attempt is made to correlate with the classifications of finds in Europe, arise

from the different materials employed—there is, for instance, no flint in South Africa,—from the absence in general of definite geological evidence, and the almost complete lack of any skeletal remains of man. There can be no question, however, that whether or not South Africa and Europe were originally contemporary in culture, South Africa subsequently lagged behind and remained Aurignacian in culture until the use of iron was introduced by Bantu immigrants, probably not more than 1000 years ago. Nevertheless, the various European cultures have their equivalents in South Africa, and the author has for convenience adopted the corresponding names, without implying that the periods in the two areas were contemporaneous. One implement of special interest which occurs abundantly in Rhodesia, and is also found in many other localities in South Africa, but rarely in Europe, is the chopping-axe or cleaver. The author brings forward strong evidence to prove that it is a finished implement.

The author gives an account not only of human remains and of stone implements, but also of Bushman paintings and their significance. A list of localities in Rhodesia where implements have been found will be of value to other investigators. It is to be hoped that this volume will prove a stimulus to others in South Africa to investigate the numerous relics of earlier times with which the country abounds.

Die elektrische Leitfähigkeit der Atmosphäre und ihr Ursachen. By Dr. Victor F. Hess (Sammlung Vieweg, Heft. 84–85). Pp. viii + 174, with 14 figures. (Braunschweig: Friedr. Vieweg & Sohn. 1926. Price 9.50 r.m.)

The phenomena connected with the electrical conductivity of the atmosphere are of importance to the physicist, the meteorologist, the geophysicist, the geologist, and the astronomer. The well-written monograph by Dr. Hess dealing with this subject is therefore welcome. It covers in general the literature of the subject up to the end of 1925, but in dealing with the penetrating radiation in the atmosphere and with the ionization of the upper layers of the atmosphere, the literature up to March 1926 has been covered. Full references are given to all the more important original publications. A detailed account is given of the investigations of the penetrating radiation of supposed cosmic origin; as a pioneer investigator in this field, Dr. Hess's account is of particular value.

The German text-books on atmospheric electricity of Gockel and of Mache and Schweidler have long been out of date. Dr. Hess foreshadows in a preface a new text-book by Prof. Benndorf and himself. We are pleased to know that such a volume is in preparation. Meanwhile, the present monograph, dealing more particularly with the phenomena connected with

ionization in the atmosphere, forms a valuable contribution to the existing literature on this subject. There are two good French works dealing with atmospheric electricity, but there is a singular deficiency of English works on the subject.

Collected Researches: National Physical Laboratory. Vol. xix. 1926. Pp. v+443. (London: H.M. Stationery Office, 1926. Price 18*s*. 6*d*. net.)

This volume contains reprints of 31 papers by members of the Staff of the National Physical Laboratory. The dates of publication of the originals range from 1917 to 1925, and the inclusion of the year 1926 in the title of the volume is therefore somewhat misleading. The papers are all concerned with physical subjects, and the originals were published mostly in the Proceedings of the Royal Society, Proceedings of the Physical Society, Philosophical Magazine, Transactions of the Faraday Society, and the Journal of the Röntgen Society. The varied subjects of the papers and the importance of many of them emphasize the number and value of the researches undertaken at the Laboratory. Each paper is prefaced by an abstract of its contents, a plan which is much to be commended. The printing has been carried out by the Royal Society printers, and is of the high quality customary of their work.

L'Energie Rayonnante. Tableaux synoptiques de l'Echelle des Longueurs d'Onde et des principales caractéristiques du rayonnement électromagnétique avec un résumé des théories actuelles. By A. Forestier. 2nd Edition. Pp. 75. (Paris: Libraire Scientifique Albert Blanchard. 1926. Price 20 f.)

This volume is concerned with the essential unity of Röntgen rays, infra-red, luminous, and ultra-violet waves, and Hertzian waves, and contains a large amount of useful information in tabular form, together with a brief theoretical outline. The introduction contains a brief sketch of Maxwell's theory and of the electron theory of Lorentz, followed by a summary of the fundamental constants. The first table deals with Hertzian or wireless waves; the second with the infra-red to ultra-violet regions. This section includes Planck's formula, photoelectric phenomena, Rutherford's atom, Bohr's theory, and Sommerfeld's theory of the fine structure of spectral lines, followed by numerical data. The third table is concerned with X-rays, including diffraction by crystals, and Moseley's law. The fourth table deals with radioactivity. The spectroscopy of gamma rays and the junction between Hertzian and infra-red rays are dealt with in a final section, covering recent work.

The volume should be useful to the student, showing, as it

does, in a simple manner the inter-relationships of electromagnetic waves of different wave-lengths. The more advanced student will also find it of value for purposes of reference.

Colloid and Capillary Chemistry. By Prof. HERBERT FREUNDLICH, Ph.D. Translated from the third German edition by H. Stafford Hatfield, B.Sc., Ph.D. Pp. xv+883, with 157 figures. (London: Methuen & Co. 1926. Price 50*s.* net.)

THIS translation of the important text-book by Freundlich on colloid chemistry is very welcome, for there is no English text-book which covers the ground in so complete a manner. The third German edition, from which the translation was made, was a reprint of the second, new matter being added in an appendix. It is to be regretted that the translator has not incorporated the additions, which amount to 30 pages, into the body of the work. Continual reference to notes at the end is annoying to the reader, particularly when there is no reference in the text to these notes.

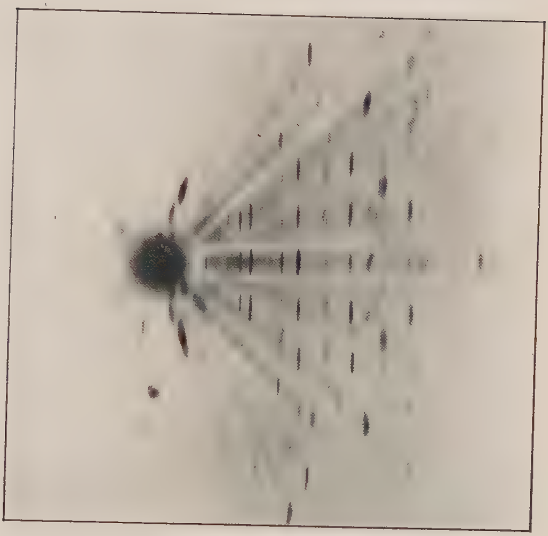
Colloid chemistry can be approached from two directions. Starting from a simple system of two phases with a common interface, the one phase can be imagined more and more finely divided and distributed throughout the other with increase of the interface. Or we may start from a pure solution and suppose the size of the particles continually increases until we come into the region of colloid chemistry. These two avenues of approach are fully dealt with in the first portion of the work. The phenomena at interfaces, or capillary chemistry, is treated in great detail. This method of treatment has the advantage that the laws governing the complicated phenomena of colloid chemistry, such as adsorption, influence of solubility, electrical effects, &c., can be more easily developed in connexion with the simpler phenomena of capillary chemistry. The processes of crystallization are fully dealt with under the heading of "The Interface Solid-Liquid." Separate sections are devoted to the kinetics of the formation of a new phase and to the Brownian movement. The latter forms the second avenue of approach.

The second portion of the book deals with colloidally disperse systems under the headings Colloidal solutions; sols (byophobic and byophylic) and gels; mist and smoke; foams; disperse structures with solid dispersion media. Experimental facts are fully described and, where possible, theoretical interpretations are preserved,

The volume is well printed and has excellent subject and author indexes at the end.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

FIG. 1.



Rotation photograph for Cæsium Alum.

FIG. 1.

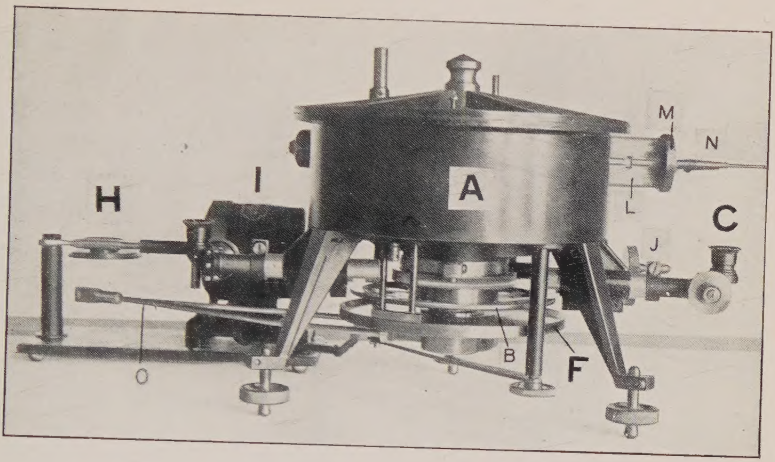
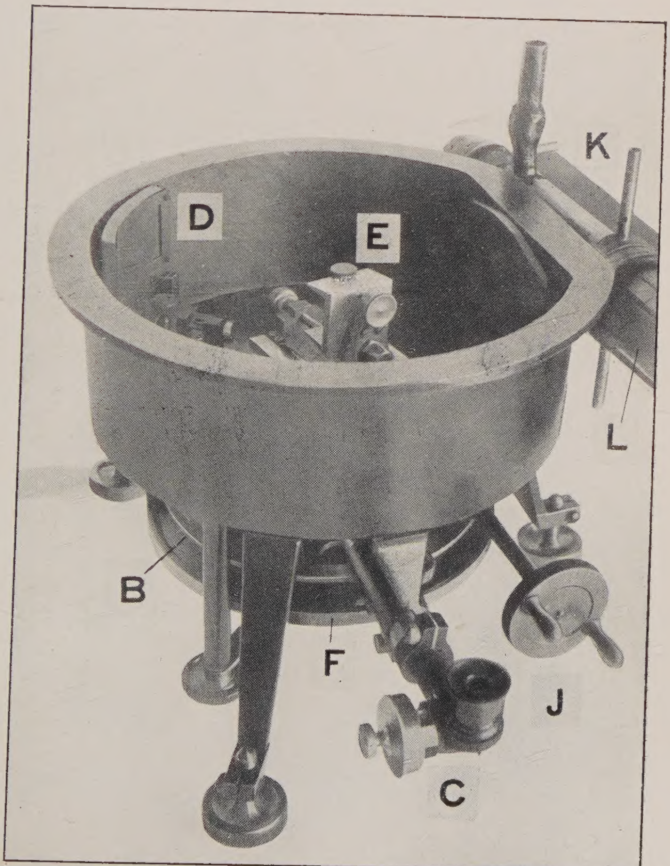
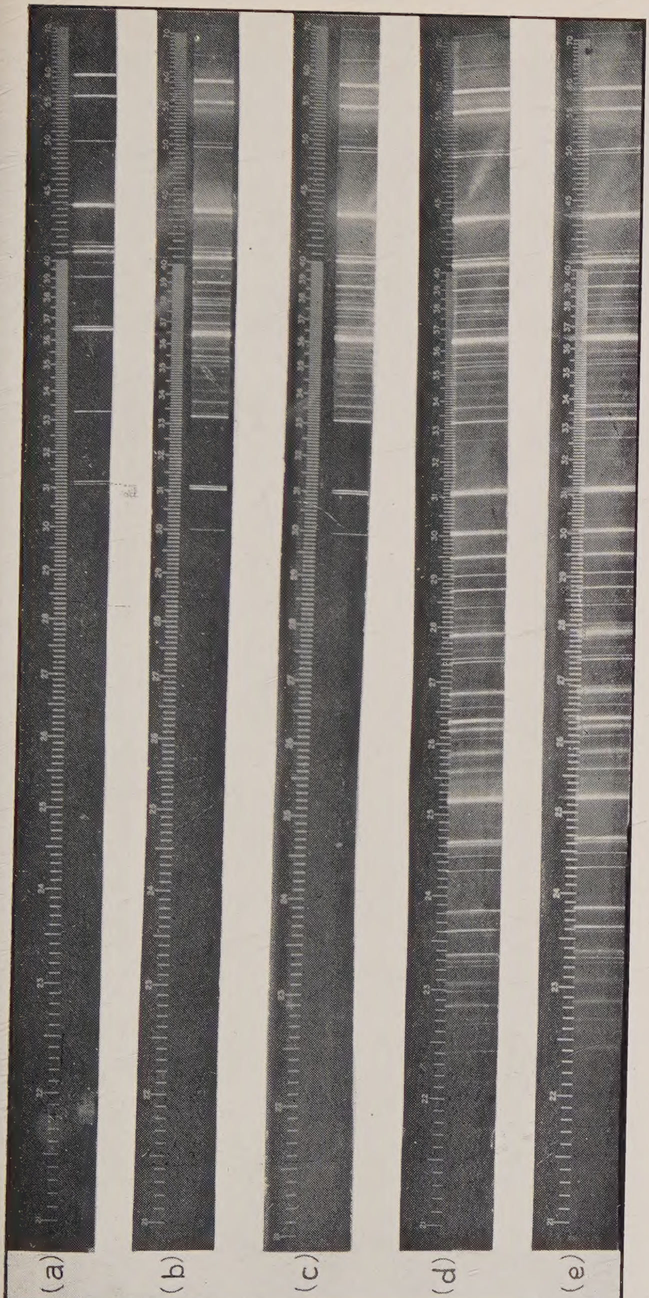


FIG. 2.





(*a*) Non-concentrated Mercury Arc in Soft Glass.
(*b*) Concentrated Mercury Arc in Pyrex Glass.
(*c*) Same as (*b*) except at Wattage Twice as High.
(*d*) Concentrated Mercury Arc in Transparent Quartz.
(*e*) Same as (*d*) except at Wattage Twice as High.